


9-2019

Environmental Assessment of Arsenic and Mercury Levels at the Garfield Mill Site, Calico, California

Steven Gregory Thorp

California State University - San Bernardino, sthorp1995@gmail.com

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ENVIRONMENTAL ASSESSMENT OF ARSENIC AND MERCURY
LEVELS AT THE GARFIELD MILL SITE, CALICO, CALIFORNIA

A Thesis

Presented to the

Faculty of

California State University,

San Bernardino

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in

Earth and Environmental Science:

Geology

by

Steven Gregory Thorp

September 2019

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Approved by:

Erik Melchiorre, Chair, Geology

George Codi Lazar, Committee Member

Kerry Cato, Committee Member

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ABSTRACT

Environmental impacts of mining at Calico, California, are poorly understood in comparison to the details of its history of silver production. Human health risks associated with arsenic from the lode rock, as well as mercury from the silver milling process, include central nervous system damage, organ failure, and death. To quantify the potential human health risk and manage remediation of this site, tailings from the Garfield Mill site were digitally mapped and chemically analyzed by portable x-ray fluorescence, which permitted volumetric estimates of total mill tailings and the arsenic and mercury budget, as well as identification of anomalies in the distribution of these elements within the tailings deposit. Final products include a high-resolution digital orthomosaic map showing the extent of the tailings deposit, giving contours of arsenic and mercury distribution and identifying areas of high concern for future remediation. The information gathered during this study will be of immense use to the city of Barstow, providing a basis for future public health studies and assessments of human health risks in the area.

ACKNOWLEDGMENTS

Thanks to the graduate committee and program coordinator for aiding with editing, guidelines, and formatting that were essential for completing this project. Thanks to Dr. Erik Melchiorre for taking me on as his graduate student and providing me this research opportunity, as well as instructing me on the various software and instruments used throughout. Thanks to Dr. George Codi Lazar for help with the mineralogy and phase aspects of this project, and for instruction on using the XRD and SEM. Thanks to Dr. Kerry Cato for help with the site map, drone work, and general guidance throughout the project. Thanks to Dr. Sterling White of the Bureau of Land Management for allowing me to conduct research on this site. Thanks to the County of San Bernardino for allowing research to be undertaken on lands under their jurisdiction. Thanks to all the staff at Calico Ghost Town, especially Derrell. for providing food, lodging, and generous hospitality for both this project and the many other times we came to Calico.

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CHAPTER ONE: INTRODUCTION

Background

As environmental awareness and concern for environmental stewardship grow, so does the importance of retracing the actions of our forebears in an attempt to correct legacy issues. The Industrial Revolution saw rapid technological, economic, and societal advancement throughout the whole world, but also made necessary a subsequent age of environmental concern. In concert with rapid economic growth during the Industrial Revolution, mining boomed during this period. When mines were abandoned owing to resource depletion or changes in commodity prices, myriad environmental and health issues were left in the wake of their closure. While modern mining corporations are held accountable for their projects and are frequently reprimanded or fined after a blunder, many older mining sites predate today's strict regulations and have never undergone the same study and scrutiny. These older abandoned mines often contain toxic secondary minerals as well as processing wastes and would benefit from being studied using the same stringent criteria as studies of modern mines.

This study mapped and quantified the silver, arsenic, lead, copper, zinc, and mercury anomalies found in the Garfield Mill tailings in the Calico Mining District, located 15 km (9.4 mi) northeast of Barstow, California (Figure 1). Elevated concentrations of silver, arsenic, lead, copper, and zinc are associated with the silver ores of the district. This study will collectively refer to these metals

as heavy metals, although arsenic is not technically a heavy metal and silver is a precious metal. Mercury was used in the processing of crushed silver ores at the mill site to increase recovery of precious metals (Lindgren, 1887). Since heavy metals other than silver were not recovered at the mill, and mercury loss was inevitable during processing, these elements would have been expelled with the finely ground rock waste as mill tailings. The extent and chemistry of these mill tailings were mapped using FieldMove software on a high-resolution base map generated from drone photographs processed with 3D imaging software.

Element concentrations in the field were measured in situ with a GPS-enabled Niton X-ray fluorescence spectrometer (XRF) calibrated to certified standards. This XRF work did not disturb the tailings. Maps of element concentration maps were generated to show distribution of mercury and arsenic within the tailings. Thicknesses of the mill tailings deposit were measured in several places where a stream cut had exposed local bedrock, which made it possible to estimate the total volume of mill tailings. With a map of element distribution, we could estimate the total mass of these elements of environmental concern within the tailings. Knowledge of the total heavy metals budget for the tailings, their distribution within the deposit, and mineral speciation will inform future work to remediate this site and protect regional aquifers and air quality. This study will be of particular use to the citizens of Barstow and Yermo who live near the mill tailings and are subjected to windborne dust from this site.

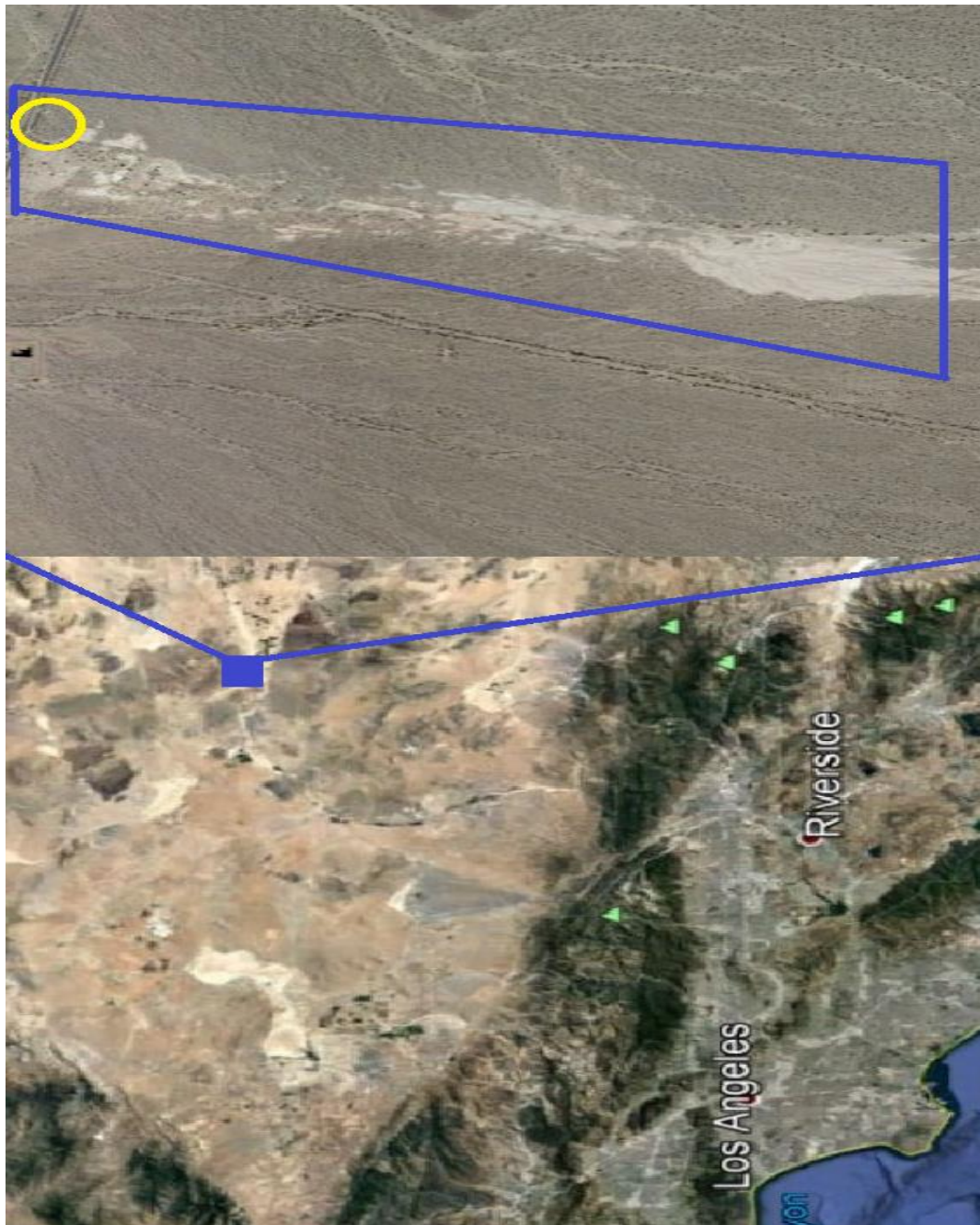


Figure 1. Aerial perspective of mill site. Subject area is outlined by blue borders. Yellow circle indicates former location of Garfield Mill site (Google Earth, 2019).

Early History

Silver was first discovered in the Barstow area in 1876 by a local prospector who initially thought he had found mercury ore. By 1880 a group of prospectors, led by local farmer and future governor of California Robert W. Waterman and geologist John L. Porter, began surveying and staking numerous claims in the area that would later become the Waterman mine (Vredenburg, 2013). This discovery encouraged other prospectors, who fanned out from Barstow and explored the surrounding desert. On April 6, 1881, another silver claim was staked 14 km (8.8 mi) northeast of Barstow by several San Bernardino residents funded by the local sheriff, John C. King. The discovery made at this site, which would later become the Silver King mine, identified masses of “horn silver” (silver chloride) at several outcrops. The initial shipments of ore sent to San Francisco assayed from \$100 to \$3,000 per ton, an extremely lucrative yield that further amplified the rush of miners to the Calico area in earnest (Vredenburg, 2013). Additional rich ore was discovered, but shipping costs to San Francisco were prohibitive.

This constraint led to a thriving teamsters business to transport ore by mule- and ox-drawn carts to the existing silver mills in Barstow for processing. Ever eager to expand their profit, early mining companies at Calico built their own mills at the Mojave River and at Daggett. By 1884 most of the ore processing occurred at Daggett.

Most of the noteworthy mines, including the Silver King, Bismarck, and Garfield, were in operation at this time, with Calico being separated into subdistricts encompassing the northern edge of the town at the base of the mountains, West Calico, and East Calico. This economic boom was short-lived owing to a sharp decline in the quality of the ore and by extension the annual output of the district. By 1886 output had been reduced to less than a quarter of the 1884 highs. The Oro Grande Company attempted to increase ore output by expanding its stamp mill at Daggett to 60 stamps, heavy iron mortars used to pulverize the ore (Vredenburg, 2013). However, this mill burned to the ground in 1887 (Figure 7).

Garfield Mill

Faced with these challenges, the mining companies realized that they needed cheaper processing near the mines. The limiting factor was availability of water, although this lack was remedied in 1886 when a high-volume well was drilled just south of town. A new mill was constructed on the site (Figure 2).

By March 1888 the Oro Grande Company began constructing a rail line from Daggett to Calico, while also rebuilding its destroyed stamp mill (Figure 3). With the introduction of small locomotives, ore-laden cars would be eased down from the steep mines to Daggett and the Garfield Mill, then return with supplies, a practice that drastically cut transportation costs to only a few cents per ton, rendering mule-driven wagons obsolete. With the mine continuing to produce only low-grade ores, by 1889 mining activities shifted from public stakes owned

by several individuals to large corporate-owned operations spanning multiple mines (Vredenburg, 2013). The Oro Grande Company bought many of the claims, and several other companies bought those remaining. It was also at this time the Garfield Mill was expanded to 20 stamps and renamed the King Mill (Figure 4).

Prosperity returned to Calico in 1890 with the passage of the Sherman Silver Purchase Act, which forced the U.S. to buy a certain amount of silver every year, causing the mining district to boom once more. By 1891 the King (formerly Garfield) Mill was expanded further to accommodate 30 stamp mills to keep up with increased production (Vredenburg, 2013). This upswing was short-lived, since silver prices dropped by almost half in 1892. By 1896 mining ceased at Calico because the profit margin was too small for local companies to continue their ventures. Several studies have listed the total silver output from Calico from 1882 to 1896 to be between \$13 million and \$20 million (Weber, 1966), but further studies believe this estimate to be low because of a lack of proper documentation and the possibility of corporate fraud (Berry, 2017).

Raw ore from the mine is first passed through a stamp mill, a motorized crusher that uses iron mortars to pulverize the ore into a fine powder or “cake”. Commonly used throughout the United States at the time, stamp mills could be set to pulverize ore to various sizes and could crush both hard and soft ores with ease. These stamps were often set to crush the ore as finely as possible to reduce stress on the stamps, a practice that increased their operating life and kept the need for repairs to a minimum (Collins, 1891). This practice also

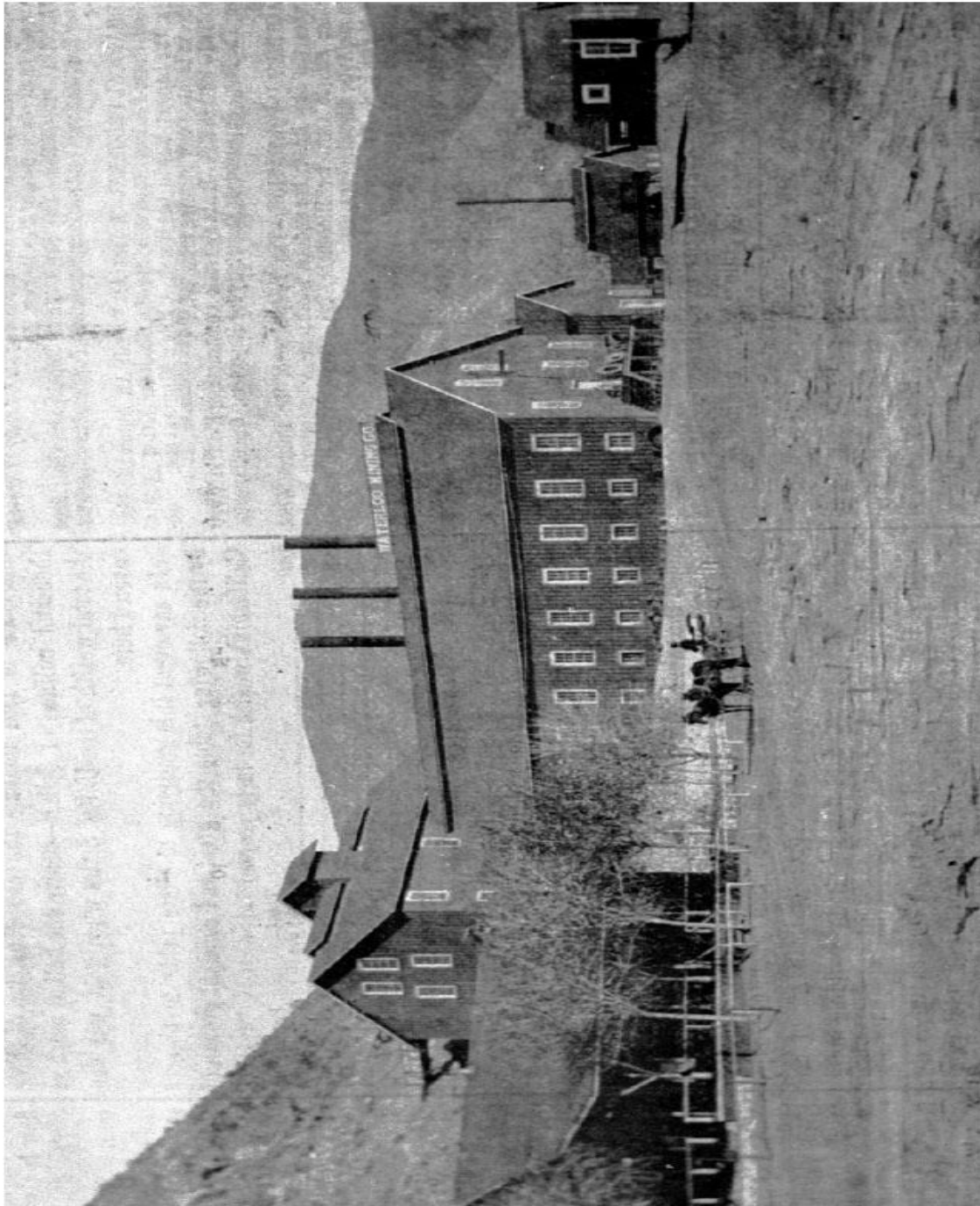


Figure 2. Photograph of the Garfield Mill upon renovation. Picture was taken in 1894 (Vredenburg, 2013).

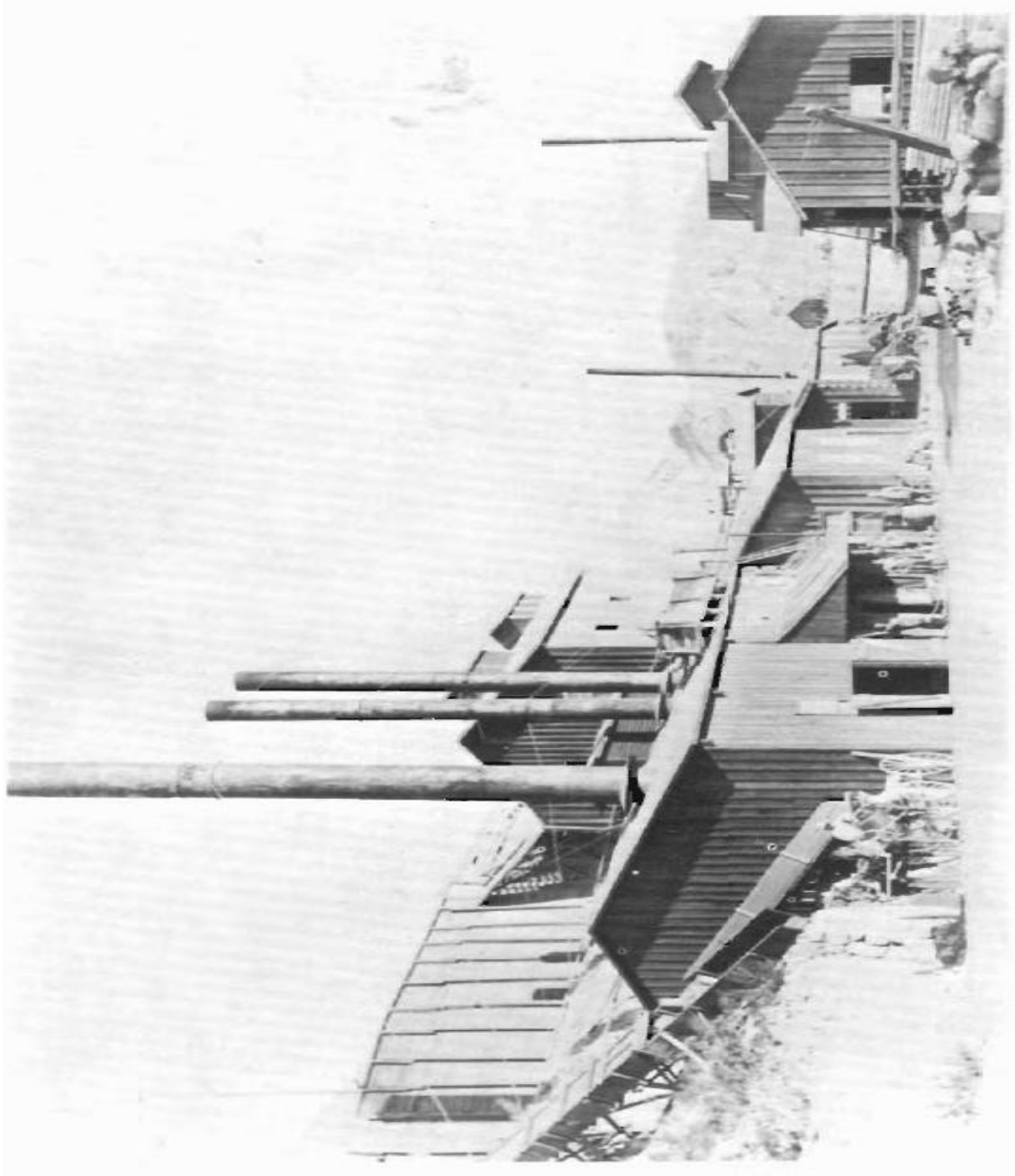


Figure 3. Photograph of the Garfield Mill. This photo was taken upon the mills' reconstruction in 1890 (Weber, 1966).

benefited the extraction process farther down the line, as the finely ground ore was more susceptible to silver extraction through amalgamation.

Raw ore from the mine is first passed through a stamp mill, a motorized crusher that uses iron mortars to pulverize the ore into a fine powder or “cake”. Commonly used throughout the United States at the time, stamp mills could be set to pulverize ore to various sizes and could crush both hard and soft ores with ease. These stamps were often set to crush the ore as finely as possible to reduce stress on the stamps, a practice that increased their operating life and kept the need for repairs to a minimum (Collins, 1891). This practice also benefited the extraction process farther down the line, as the finely ground ore was more susceptible to silver extraction through amalgamation.

At the Garfield Mill, the “stamped” and pulverized ore was then treated by the M.P. Boss Process (Lindgren, 1887), an industrialized, continuous extension of the Washoe Process. Used extensively in the processing of gold and silver ore, the Washoe Process consists of first crushing the ore as small as possible using a grinding pan, either hand-operated or motorized, using both wet (by adding water to facilitate easier grinding) and dry variants (Collins, 1891). In the case of crushing soft and rich silver ores of chloride and sulfide such as those found at Calico, it was found that crushing ore using a dry method in the initial pan-crushing phase yielded a higher recovery rate than the wet variant (Collins, 1891), although the operating costs of doing so would be outweighed only with

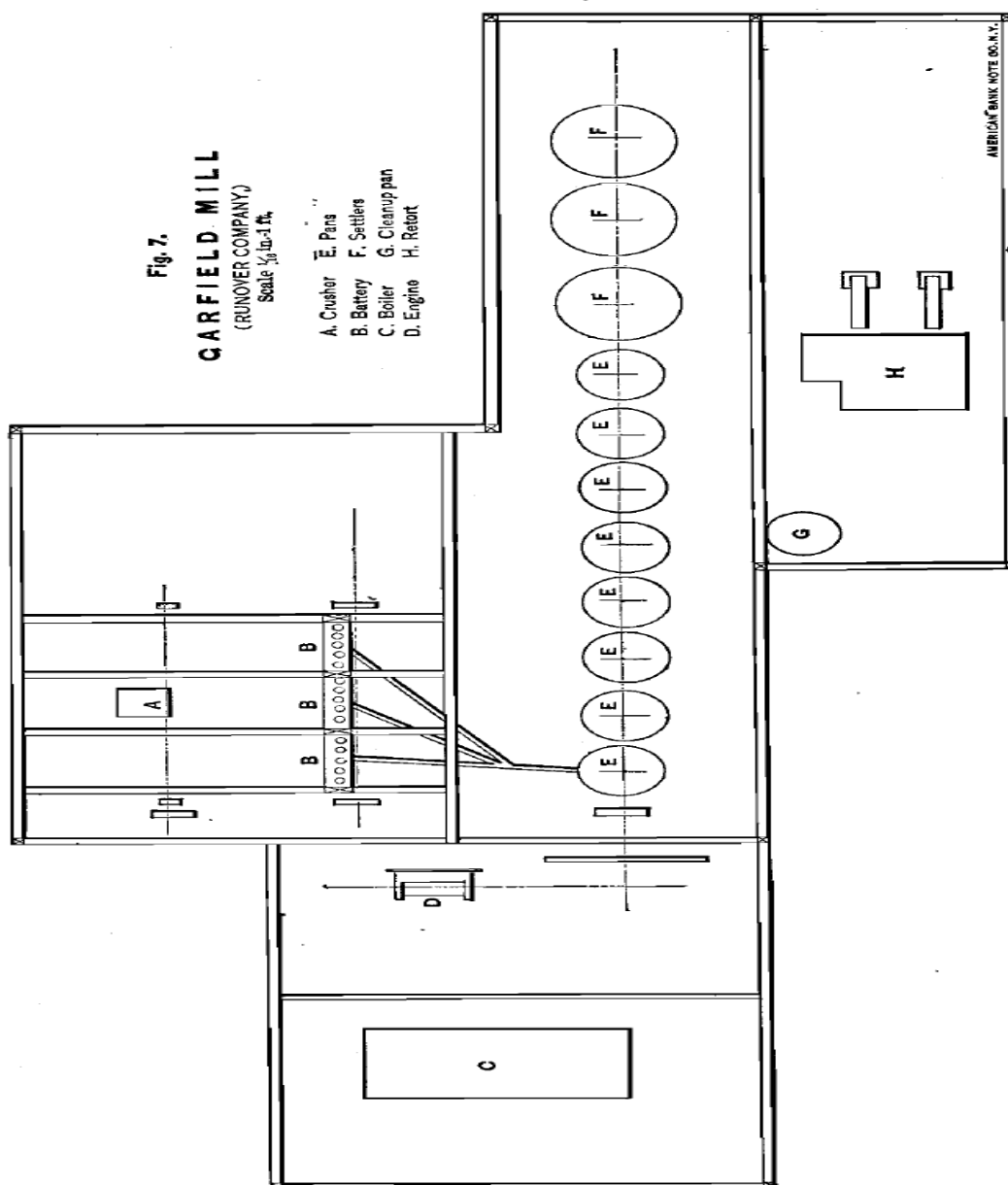


Figure 4. Layout of the Garfield Mill. Lindgren (1887).

high-quality ores. Crushing the ores with the wet variant of pan crushing was often more efficient when dealing with the lower-grade ores encountered in the latter half of Calico's mining period, since the silver loss from the slimes involved in extraction was compensated for by the sheer volume of ore processed. Collins (1891) mentions that silver ores accompanied by arsenic- and lead-rich sulfides would benefit from being pre-roasted with salt before crushing to increase extraction efficiency, but this method was not used at Calico because the gains in silver were outweighed by increased processing costs.

At the Garfield Mill, the crushed low-grade ore was typically poured into revolving pans filled with mercury and small amounts of water, which caused it to be considered the "wet" variant (Collins, 1891). The pan was then spun and heated with steam to force the mercury amalgam to mix with the silver-bearing ore, which eventually coalesced into globules that were ejected from the pan into a settling bin. The remaining amalgam would then flow into a second pan; the process would be repeated several times (depending on the number of pans present in the mill) to ensure maximum amalgamation of silver and by extension increased silver yield. The leftover amalgam was then strained through a canvas lining within a large box, which allowed the mercury to drain through the pores in the liner by its own weight, although the remainder was often squeezed manually once or twice to expel the rest (Collins, 1891). The remaining pasty amalgam would then be added to the mercury pans for a second run or ejected with the tailings, since this material was usually contaminated with high levels of lead, sulfates, arsenic, and other unwanted elements that had bonded to the mercury.

The amalgam that had drained successfully would then be processed by heating to separate the volatile mercury from the silver. The mercury vapor would be condensed and reused, while the extracted silver would be formed into large ingots.

While silver extraction efficiency at Calico was high, averaging 80–90% (Lindgren, 1887; Collins, 1891), various chemical, mechanical, and human factors joined to reduce efficiency at the mill. As mentioned earlier, the presence of arsenic- and lead-bearing sulfides would make additional ore processing via salt roasting necessary before crushing could even begin; this process was not used at the Garfield Mill owing to resulting higher costs. The ores and lode rock present at Calico often contained arsenic minerals within the barite ore.

Silver loss from ejected amalgam was inevitable, since it wasn't economically feasible to remove every ounce of silver; however, the amount of silver loss increased when the ore was milled alongside certain elements. The chief source of mercury loss in the Washoe Process was mechanical, i.e., spilling and splashing the mercury during handling, so much so that large quantities can often be found in the foundation of the mills (Collins, 1891). The principal mechanical source of mercury loss was from the ejection of "floured" (emulsified) mercury along with the mill tailings from the amalgamation pans. Flouring occurred more often when the mineral contents interfered with amalgamation, which caused the globules that were formed and subsequently broken apart by the grinders to be less likely to reform and thus to be ejected with the tailings. These losses increased further with ore particulate size, since larger material

was less susceptible to amalgamation, which is why the stamp mills were often set to pulverize them to very fine sizes. Chemically induced losses of mercury were minimal, since the process involved exposing the amalgam to large amounts of reducing agents, salts, and potassium cyanide (Collins, 1891), which kept the process more efficient, or “lively” in the older literature.

Interference by various substances was another concern, as many minerals could make the mercury “dirty” by coating the amalgam globules, which both limited their ability to amalgamate and increased mercury loss at the mills. Collins (1891) referred to such substances using the general term “grease,” which included (but was not limited to) substances such as steam exhaust, talc, kaolin, and various hydrated silicates. Each had similar effects by covering the surfaces of the globules. Iron shavings and graphite from normal wear and tear of the mill stamps would also cause such reactions, so both the mill stamps and mixing pans were cleaned and maintained regularly to reduce the total iron available in the mercury solutions.

While mechanical properties were the primary cause of mercury loss, interference by other ores had many effects on amalgamation. Copper ore was found to enhance amalgamation (Collins, 1891), while lead- or arsenic-bearing ores greatly hindered it. Lead minerals would contaminate the mercury by rapidly amalgamating into a pasty, easily tarnished amalgam that floured readily and caused great losses (Collins, 1891), although this effect also depended on the lead minerals involved. Cerussite (PbCO_3) and galena (PbS) were found not to affect the process, while wulfenite (PbMoO_4) would cause the pans to expel the

floured mercury in significant amounts. This effect is believed to be caused by the precipitation of lead by iron-oxide shavings, although certain species of lead were virtually immune to this process.

Arsenic minerals such as proustite, arsenopyrite, and arsenic-contaminated barite were especially hard on the amalgamation of mercury. The mercury would not only flour but was also “sickened,” which would cause it to not readily amalgamate (Collins, 1891). These two effects would enhance each other and cause the mills to hemorrhage mercury with the tailings. In modern mining projects, even within the gold industry, arsenic removal from ore is a tedious process. At the gold mines of southern Canada, whose gold ores were also rich in arsenic, the element had to be removed at great cost, with subsequent environmental effects still plaguing the area.

Lastly, mercury loss would have occurred due to human error, during both normal operation and corporate shifts. As mentioned earlier, Calico went from a collection of many personal claims by groups of individuals to only a handful of claims held by large corporations. It is quite possible that corporate shifts and the subsequent switching of personnel increased mercury loss, both unintentionally because new crews had to learn the systems or possibly even intentionally via sabotage by individuals who had lost their job during such switches. While this cannot be proved, it is still likely and should be considered in terms of mercury loss sources, since at the time a single container of mercury would have been worth \$75 (Lindgren, 1887), a steep price to pay because of the breakage of a single container.

The Cyanide Leaching Era

By the turn of the 20th century the Calico Mining District had all but ceased activities because the price of silver had dropped steadily since 1894, to a low of 64 cents per troy ounce. Most of the mines had closed in hopes that silver prices would rise once again, while a few remained active with a fraction of their previous work force. From 1900 to 1915 the district remained nearly dormant, as the price of silver continued to drop (Weber, 1966). Silver prices experienced a temporary rise between 1915–1919 and reached \$1.38/oz owing to industrial and monetary demands during and directly after World War I. But the price fell once again over the following decade.

Although silver prices were less than optimal for direct primary mining from bedrock, the District saw renewed activity and production during this period, with cyanide leaching of mill tailings that had been produced by prior mining and milling activities. Tailings were reprocessed by the Calico-Odesa Company, Zenda Mining Company, and the Daggett Reduction Company, as well as several smaller operations, including Larry Coke and his wife, the caretakers of Calico in the 1940's and 1950's. These operations produced an estimated 250,000 troy oz (about 8.5 tons) of silver (U.S. Bureau of Mines, 1933–1995; State of California, 1879–1925).

Cyanidation techniques had never been used extensively at Calico, as this newer method was not invented until 1887, and mines in California didn't adopt it until 1891 (Weber, 1966). The process involved the use of cyanide (usually as

Na or K compounds) to dissolve ground ore and extract the silver and gold content. The process was first used industrially by, and its invention credited to, John Steward MacArthur and brothers Dr. Robert and Dr. William Forrest of the Rand Company of Scotland (McLachen, 1933), culminating in the MacArthur–Forrest Process. The process rendered gold and silver soluble and thus easily leached from solids. The precious metals-rich cyanide solution could then be stripped of silver and gold through electrolysis or by precipitation using zinc or various salts. Early testing by MacArthur yielded gold extraction efficiencies of up to 96% (McLachen, 1933). These efficiencies enabled low-cost production of gold and silver from mine dumps and tailings piles across the nation.

By 1900 the process had been improved by several individuals, with the Merrill-Crowe Process being the most recent improvement within the U.S. This process added several additional steps to the original MacArthur–Forrest Process, such as the use of zinc dust in precipitating gold and silver, running the solution through a vacuum chamber to remove excess oxygen in solution, the use of another vacuum to pump air into the solution to increase precipitation, use of filters to remove precipitated gold, silver, and zinc dust from solution, and sulfuric acid to dissolve the zinc dust but retain the gold and silver.

Although originally invented to extract gold, the process was used to remove various other precious metals, including silver. The Daggett Reduction Company, one of the most productive operations of this type, began using cyanidation to reprocess the Garfield Mill tailings from 1915 until the late 1930's (Weber, 1966). Silver extraction from the tailings was economically feasible

owing to the inefficiency of the original methods used by mills at Calico. The Garfield Mill was reported to be only 80–95% efficient, depending upon ore type being milled (Lindgren, 1887; Collins, 1891). This produced mill tailings that ranged from one to tens of ounces of silver per ton (Weber, 1966). Potassium cyanide was the chief leaching solution used during this time. Cyanide leaching techniques remained in use at Calico until 1963, when all industrial mining efforts ended because of lowered profit returns from the tailings. Studies by Agey (1973) and Kudryk (1970) were later conducted to evaluate the validity of Calico's ore deposits as viable silver sources if mined with more modern cyanide leaching techniques (Weber, 1966).

Modern cyanidation techniques built upon older variants with the addition of roasting the ores/tailings in salt before processing or subjecting them to an additional grinding stage to reduce grain size even further. Both methods yielded higher silver extraction efficiency than their predecessors, with fine grinding methods ensuring a minimum of 60–65% extraction of silver, and salt roasting extracting more than 80% of silver (Agey, 1973). Extraction of barite alongside silver was also proposed for the updated cyanidation techniques to reduce profit losses due to processing costs through the sale of extracted barite. The prospect of continued silver mining using such techniques was ultimately abandoned because profits were economically unattractive and demands to preserve the historical aspects of the district were increasing, which has left the Calico Mining District bereft of industrial activity ever since.

Geology

The bedrock geology of the Calico area is dominated by the sedimentary Barstow Formation and the igneous Pickhandle Formation (Figure 5). The silver ore deposits are limited almost exclusively to the Pickhandle Formation. Many faults of varying age cut these rock units. The more recent geologic deposits are divided between Quaternary alluvium and Anthropocene mill tailings. Lindgren (1887), Weber (1966; 1967), and Vredenburg (2013) have previously written on Calico's geology, each detailing the presence of chlorides and chloro-bromides of silver as the primary silver-bearing minerals, with a gangue (waste mineral assemblage) of barite. Figure 5 shows the stratigraphy of Calico.

Pickhandle Formation

The oldest rocks exposed in the Calico area are the Miocene volcanic rocks of the Pickhandle Formation (Jessey, 2010). This formation is a sequence of pyroclastic rocks roughly 1,493 m (4,900 ft) thick that rest upon the Jackhammer Formation conformably and are unconformably overlain by the Barstow Formation (Dibblee, 1968). The Jackhammer Formation is not exposed in the field area. The Pickhandle Formation is the most diverse geologic body in the area; its northeasterly to westerly trend makes up most of the southwestern and northern corners of the mining district. Dibblee (1968) describes the formation as consisting of, in order of increasing depth, granite conglomerate, hornblende andesite tuff breccia, quartz monzonite breccia, sandstone tuff, a

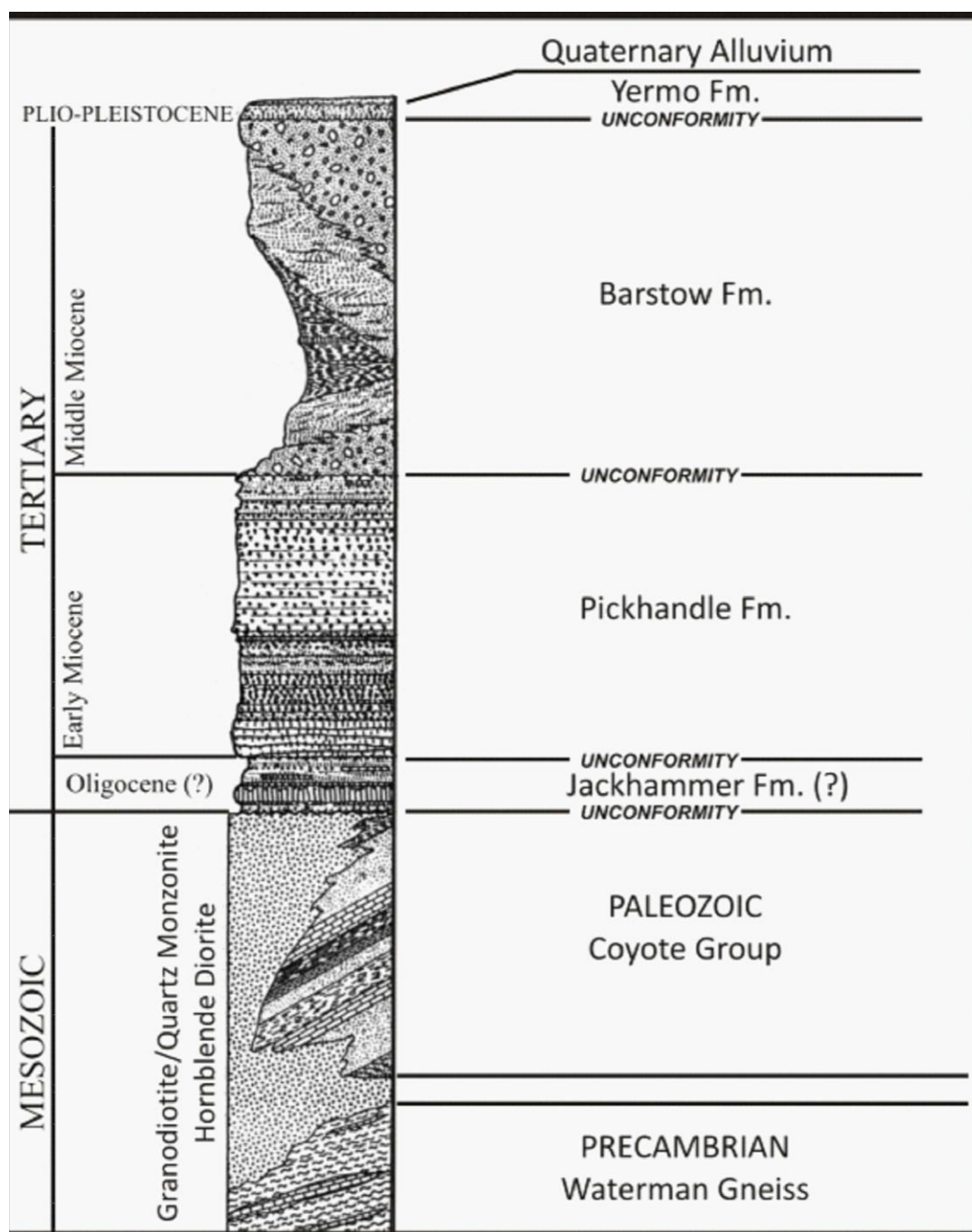


Figure 5. Generalized stratigraphy and formations of Calico. (Jessey, 2010).

second unit of quartz monzonite breccia, dacite tuff breccia, and a second unit of tuff/tuff-breccia. It is believed to have been produced by the deposition of sediments and volcanic materials on a large, steep Miocene mountain slope that led to a granitic highland. Further deposition of remobilized tuffs and quartz monzonite are believed to originate as stream deposits that occurred during the time. This formation has a characteristic “pocket” weathering habit, which miners used to create shelters (Figure 6). Its wide range of colors from green to red (Figure 7) reminded miners of calico fabric, and this concept gave the district its name.

Barstow Formation

Lindgren (1887) noted that the Calico Mining District is surrounded by great geological bodies of “sandstone” that make up the vast majority of the surrounding Mojave Desert. This Barstow Formation consists of fossil-rich stream-laid sandstones, mudstones, and conglomerate alongside limestone and other rocks. The Barstow Formation is believed to have originated during the middle Miocene as the result of depositional erosion from pyroclastic materials within the Pickhandle Formation and a nearby granitic mountain range (Weber, 1966; Woodburne, 1990). Local uplift that produced the source areas for these conglomerates, mudstones, sandstones, and carbonates also caused the adjoining basin to subside (Dibblee, 1968). Increased volcanic and tectonic activity in the Late Miocene led to the creation of rugged granitic and volcanic highlands that continuously deposited sediment into the Barstow depositional basin; this process ultimately created the formation, alongside Miocene streams



Figure 6. "Pocket" (large deep voids) weathering habit of the Pickhandle Formation. Here, miners enclosed a pocket large enough to be used as a domicile.



Figure 7. Picture of Calico mountainside. The mountainside vividly displays the red and green minerals easily identified by miners at the time. that deposited deltaic sands into the basin.

The Barstow Formation ranges from dull red to gray-tan sediments, characteristically spectacular anticlinal and synclinal folds (Figure 8). Woodburne (1990) provides a comprehensive review of the Barstow Formation and its three main sub-units.

Hornblende Andesite

This unit is restricted to a few small hills to the south of the town of Calico, at the site of the Garfield Mill (Figure 9). This reddish to gray-brown volcanic unit is porphyritic with plagioclase and hornblende phenocrysts in a microcrystalline groundmass (Dibblee, 1968). It is heavily brecciated locally. This unit is believed to have formed after the Pickhandle and Barstow Formations, and to have provided the heat source for generating the silver-mineralizing fluids (Webber, 1967).

Quaternary Alluvium

The flat topography to the south of Calico is dominated by Quaternary alluvium that slopes very lightly from the Calico Mountains south toward Interstate 15, before sloping upwards again towards the opposing mountains that constitute Yermo's surroundings. The alluvium is tan to brownish-tan, with a texture that resembles sandy loam or possibly sandy silt. Some localized zones of coarser gravels may be present, especially closer to the mountains. Roughly 0.5 km to the south of the Garfield Mill, within the alluvial unit, lies a dry lakebed of fine-grained silt, mud, and evaporate minerals.



Figure 8. Folds of the Barstow Formation at Calico. Students are used for scale; student on far left is 6 ft tall.

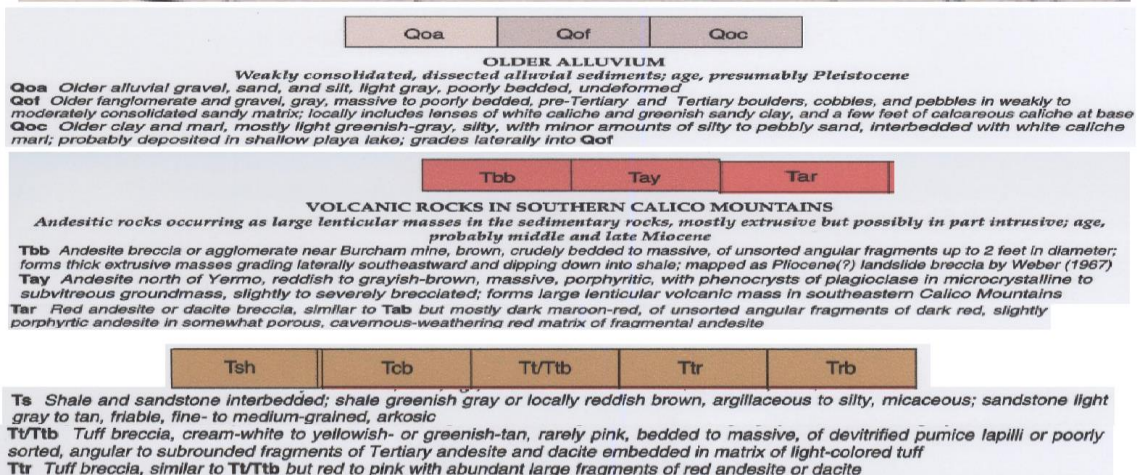
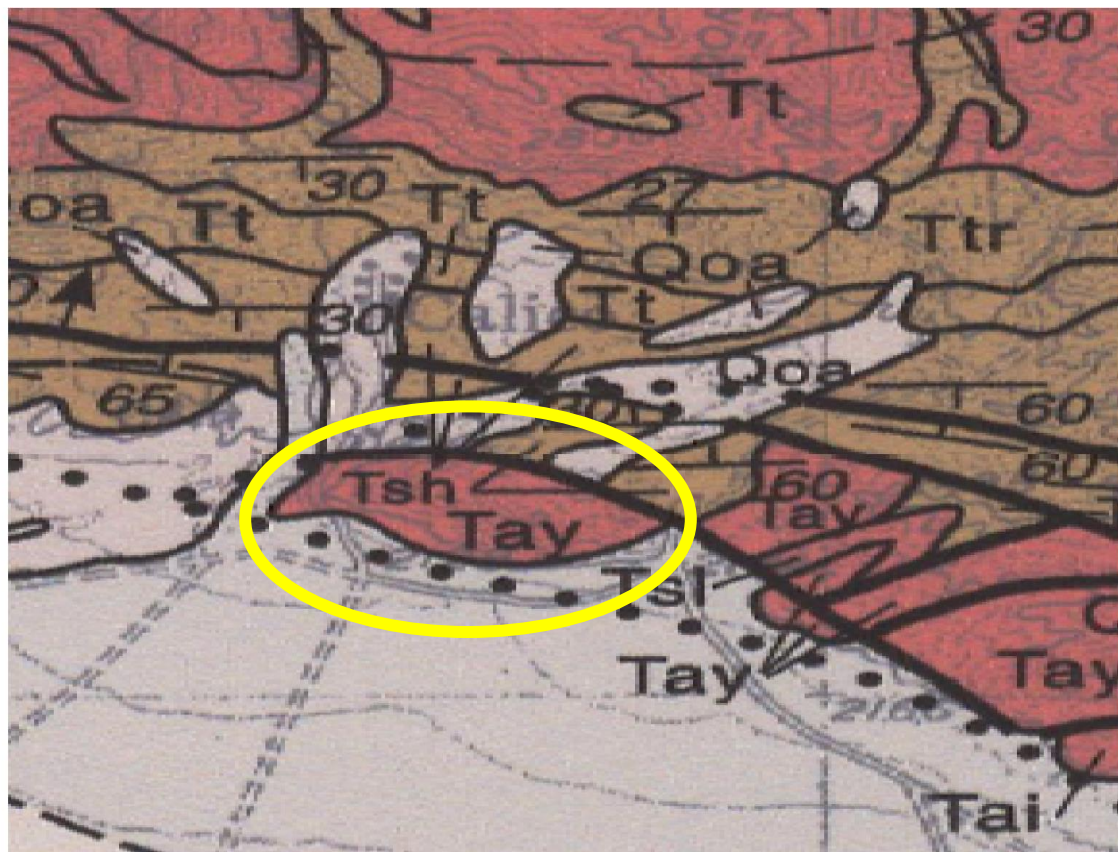


Figure 9. Geologic map of the Calico Mining District. Yellow circle indicates the location of hornblende–andesite body (Lindgren, 1887).

Anthropocene Mill Tailings

The mill tailings around the former Garfield Mill site extend 1 km south from Ghost Town Road, with a maximum width of 0.2 km. The tailings differ greatly from the surrounding desert alluvium and are easily seen from high altitudes, displaying a wide array of colors. The majority appear white to white-tan, with pockets of red, gray, purple, and gray-green appearing throughout (Figure 10). The coloration appears dictated by the presence and oxidation of iron-bearing minerals. The mill tailings consist of laminated depositional layers of sand to silt-sized sediment that was produced by crushing at the mill. This material often occurs as a fine dust or clump “cakes.” The texture and cementation of the sediment vary between individual piles, with some piles being heavily cemented by secondary minerals, requiring a rock hammer to break and often fracturing into sizeable chunks. Other piles are extremely friable, cracking easily under slight pressure and disintegrating into a fine silty dust that is easily swept away by the wind. Some areas in between the larger piles have undergone little to no cementation and exist as very fine grained, soft, and powdery piles of tailings.

Interestingly, many of the larger and well-cemented piles exhibit well-defined micro-stratigraphy, the layers changing in color and texture greatly from one to the next (Figure 11). These piles tend to be stable but friable, loosely resembling mudstone varves. Colors resemble the general tailings, though lighter shades of gray, tan, brown, and red are more common, with some piles

containing thin but well-defined layers of yellow material.

Several stockpiles of rock around the remnants of the mill's concrete foundations (Figure 12) consist of unprocessed silver ore from the mines, ranging in size from gravel to small cobbles. These piles are mostly tan-red (barite ore/sulfides), gray-black (manganese/lead sulfides), and green-gray (copper sulfides and chlorides) never more than two meters in diameter and one meter in height for a given pile (Figure 13). Hand samples of a black, lustrous, columnar, and slightly striated arsenopyrite could be found at several of these piles.

The northern end of the tailings on the opposite side of Ghost Town Road, hugging the old train trusses and the perimeter of the former mill site, was also rich in a black rock believed to be oxides of manganese and smelter slag (Figures 14A and 14B). The material is gravel-sized angular black clasts in a finer-grained black to gray matrix. The pile sloped up from the road at a height of roughly 5.5 to 6 m, plateauing at the top abruptly from a road cut. This relationship suggests that this material was imported for construction of the road and railroad grade and is likely smelter slag.

At the southernmost end of the tailings lies a massive pile of tailings that dwarfs the rest, referred to herein as the "Behemoth Mound" (Figure 15). The Behemoth Mound is white-tan, the most cemented unit within the site, and stands at 0.25 km long, 0.2 km wide, and 5–6 m in height at its tallest point. This pile is believed to be a stockpile of tailings at the site of the cyanide leaching operations during the early to mid-1900's. Bulldozers probably helped create this mound, as

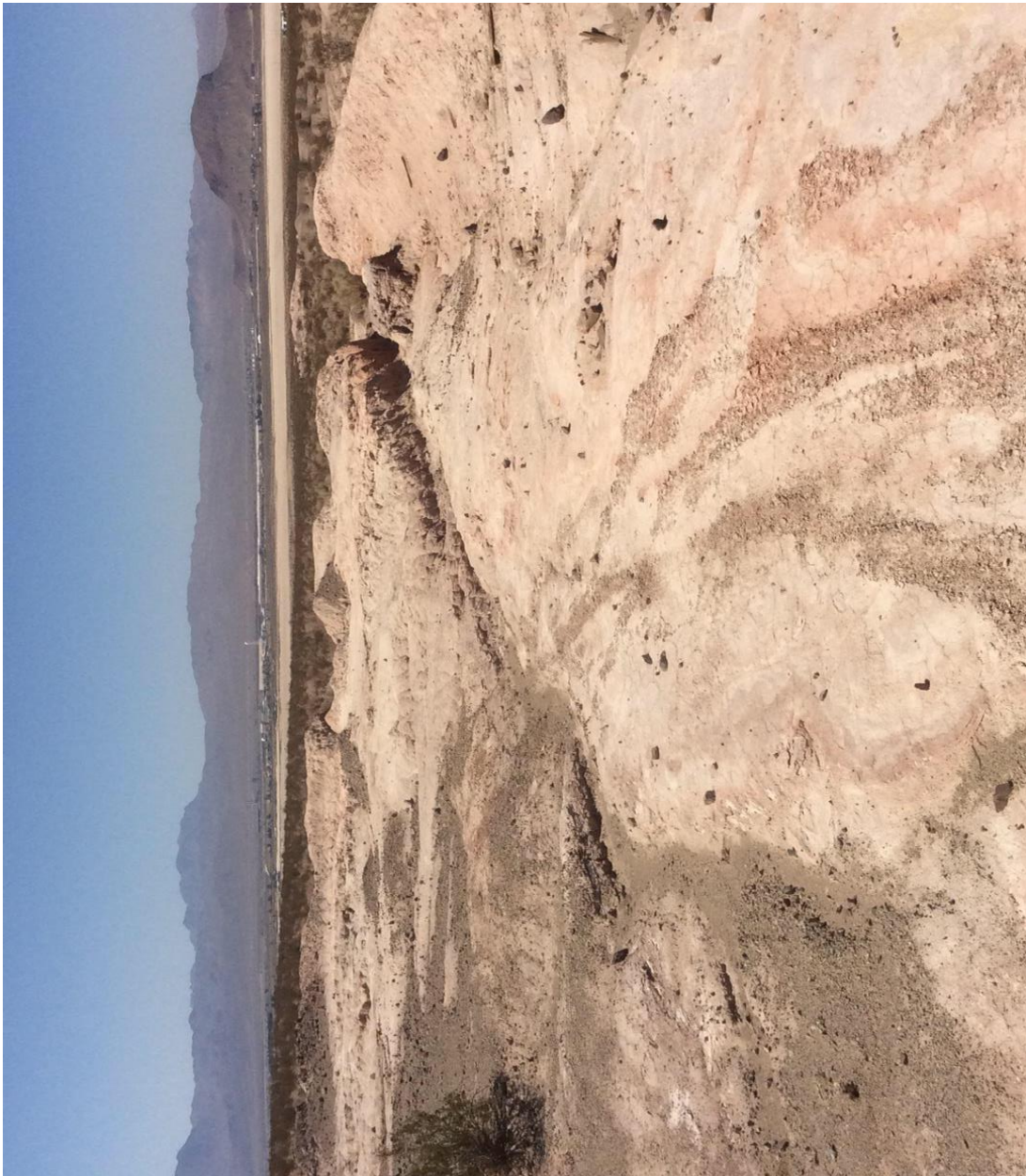


Figure 10. Tailings pile within the upper right section of Sector 1 of the Garfield Mill tailings. Note the varying coloration and cementation.



Figure 11. Micro-stratigraphic layering of well-cemented tailings piles. Found within Sector 3 (top) and sector 1 (bottom) of the Garfield Mill tailings. Note differences in coloration and cementation between layers. Photograph taken November 2018.



Figure 12. Concrete foundations within the mill site. Examples of surviving concrete foundations of the Garfield Mill (top, Sector 1) and later cyanide leaching plant (bottom, Sector 4). Photographs taken November 2018.



Figure 13. Rock and gravel pile consisting of unprocessed ores. This subject was located on the border between Sectors 2 and 3. Photograph taken November 2018.



Figure 14A. Northern section of Sector 1 of the Garfield Mill tailings. Located across Old Ghost Town Road, this was the location of the mill site, beneath the train trusses (upper right). Photograph taken September 2018.



Figure 14B. Aerial drone photograph of mill site. This photo is an aerial closeup of the original mill site within Sector 1, north side of Old Ghost Town Road, Calico. Photograph taken August 2018.

the coherent layering seen elsewhere in the tailings is absent.

Economic Mineralization and Faults

The silver ores of Calico exist primarily within fractures and dislocations of local faults such as the Calico Fault. These silver-ore deposits were formed from the intrusion of aqueous hydrothermal solutions that filled these fractures and dislocations before overflowing near the surface (Lindgren, 1887). This pattern of upward deposition by aqueous solutions heightened the concentrations of silver near the surface and explains the lack of economically viable silver deposits at lower depths. This conjecture is further proved by the fact that few of the mines at Calico found ore deposits of great value beyond a depth of 200 ft, although the gangue deposits stayed uniform in silver concentration at all levels of the mines (Lindgren, 1887).

Weber (1966) notes that the Silver King mine had reached depths in excess of 500 ft with silver content remaining uniform in concentration. The presence of silver outcrops at the surface also suggests that upon filling the fault fractures the solution would overflow upward towards the surface, so much so that the miners originally thought the silver had been deposited on the surface and had then flowed downward into the fractures. Surprisingly, this hypothesis is partially true in that the Calico mineral deposits experienced secondary deposition from the action of downward-moving meteoric water from the surface. This downward flow of rainwater through the fractures in the mineral bodies stripped some of the silver from them, then deposited them farther below at lower

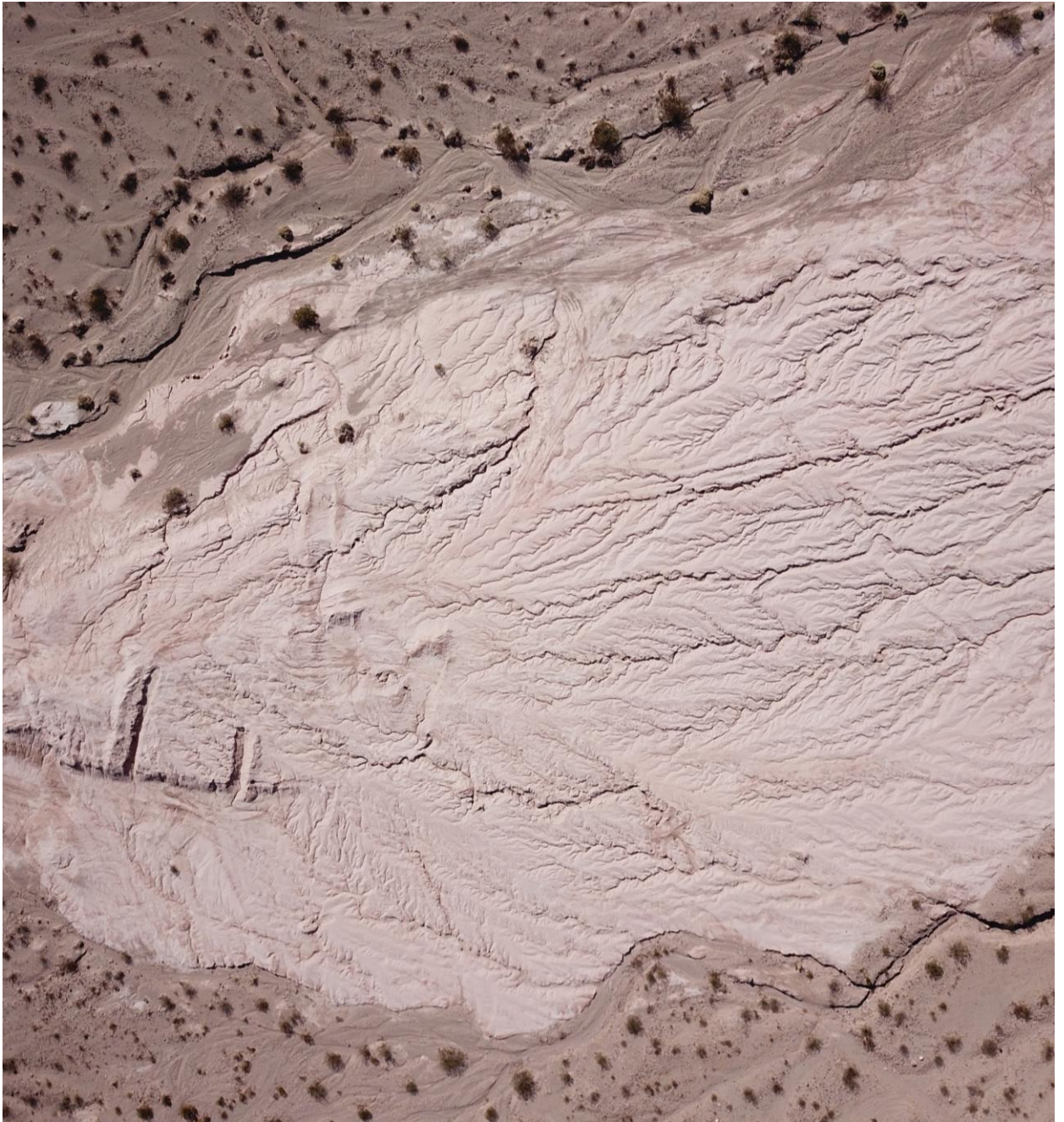


Figure 15. Aerial drone photograph of the Behemoth Mound. This single mound makes up the majority of Sector 4 of the Garfield Mill tailings. Photograph taken August 2018.

depths, roughly 170 ft to 240 ft. This process resulted in secondary enrichment of the lower ore bodies and allowed far more silver to be deposited in the area, adding millions of dollars of silver that increased the enormous profits made at the District (Weeks, 1929).

The formation of these deposits by thermal springs is further supported by numerous silver mines throughout the western United States that share Calico's depositional characteristics, such as the Comstock Lode of Nevada and the Bodie and Panamint mines of California. The aqueous solutions that yielded the ore deposits probably sourced the ore and gangue material from the eruptive rocks located deeper within Calico's stratigraphy, then deposited them upon the surface and the tufa beds.

Lindgren (1887) identified silver-barite deposits located upon beds of tufa and rhyolite (referred to as liparite in the older literature) as Late Tertiary in age. They follow the trend of many ore deposits in the west which were sourced from eruptive rocks, although such deposits are usually Pre-Cretaceous to Cretaceous in age. Upon filling and then overflowing the vein fissures, the solution is believed to have receded down to the pyroclastic rocks and below. This process resulted in the first round of secondary enrichment that occurred at the ore bodies, with the rest believed to have been caused by surface water flowing downward through the fissures. The mineralization of silver-bearing ores and gangues at or near the surface by these thermal springs translated into reduced operating costs for the mining operations at Calico. They were also the chief cause of the "boom and bust" ore output that ultimately led to the decommissioning of mining

activities, since ore value correlated negatively with depth and increases in operating costs, a diminution that was further crippled by the later sharp decline in silver prices.

The Garfield mine was found to be unique in the district owing to the presence of a high quantity of copper sulfides, copper-bearing chrysocolla, and (rarely) malachite (Lindgren, 1887). Rhyolite is present throughout the Garfield mine, with silver ores often present in the cracks and fissures within the rhyolite bodies. Lindgren (1887) proposed that hydrothermal systems in the form of thermal springs were responsible for impregnating rhyolite fractures by the silver ores, and states that this is further proved by the presence of silver-rich barite-bearing rock both on the surface and within lower-level rock.

Previous Work

The history, geology, and economic mineralization at Calico has been the subject of numerous studies (e.g., Lindgren, 1887; Weber, 1966; Weber, 1967). None of these studies focuses on detrimental environmental effects from mining. The only elements discussed in detail in these early reports were silver and barium, due to their economic significance (Weber, 1966). Similarly, more modern work done by Ochart (2015) and Berry (2017) focused on the total amount of silver extracted from the mines, since there has been evidence of corporate fraud having occurred at Calico with respect to reporting of the mines'

true silver output. This work has narrowed down the gross amount of silver extracted: estimated to have been more than \$40 million, almost double what was reported on official records. Using this information, the profits from silver can be repurposed into gross weight of silver extracted, and when this value is combined with ore samples from the site, which give insight into the ratios of silver to lode rock, a gross estimate of the total amount of material extracted from Calico can be generated. Previous studies primarily covered the silver output of the mines (Berry, 2017), the surrounding geology (Lindgren, 1887), its history (Vrendenburgh, 2013), or a mixture of all three (Weber, 1966).

Significant quantities of mercury, referred to as “quicksilver” in the older literature, were used in the mill process to recover silver from crushed ore (Lindgren, 1887; Collins, 1891). However, the mills did not recover the arsenic associated with the silver-bearing ores, and no mention is made of this element other than to cite its detrimental effect on silver recovery (Collins, 1891). These fine-grained mill tailings and associated mercury and arsenic have the potential for windborne (aeolian) transport as dust, and the potential for rainfall to physically mobilize them through riverborne (fluvial) means (Kim, 2014). Aeolian transport is the recognized primary method of arsenic mobilization in semi-arid climates, while fluvial transport results in heightened concentrations along narrow gulches formed from sporadic rainstorms (Kim, 2014). The environmental effects of arsenic and mercury contamination are well documented. Both have very high bioaccumulative tendencies and severe adverse effects on freshwater aquifers when released by chemical weathering (Chakraborti, 2015; Chowdhury, 2018).

Specifically, arsenic exposure produces a plethora of assaults upon the human body that affect the nervous, cardiovascular, endocrine, reproductive, and dermal systems (Figure 16). It is a known carcinogen and a cause of peripheral neuropathy, Blackfoot disease, and diabetes (Abdul, 2015). The endocrine systems of children are especially susceptible to arsenic poisoning, causing reduced growth and affecting the maturation and functions of the pancreas, reproductive organs and prostate, as well as brain development during puberty (Abdul, 2015). The deleterious effects of arsenic on both the environment and human health has been well documented in the last three decades owing to the human health crisis in Bangladesh, which resulted in contamination of more than 70% of the country's water supply with lethal amounts of arsenic. Arsenic was used in wood preservation in the 20th century, but increased knowledge of its toxicity has since diminished its use in most industries aside from electronics, where it is commonly used to make high-quality semiconductors. Holland et al. (2005) provides an extensive overview of the many properties, reactions, and behaviors of arsenic within natural cycles. The article also covers the many properties of mercury within nature, including its associated health risks and environmental effects.

Mercury poses a significant health risk and is a documented cause of miscarriage, prenatal brain deformation, and severe damage to the central nervous system and kidneys (Ha, 2017). The primary method of transport for mercury is aeolian, usually following combustion such as in coal-burning power plants (Ha, 2017). Concerns over fluvial contamination and subsequent transport

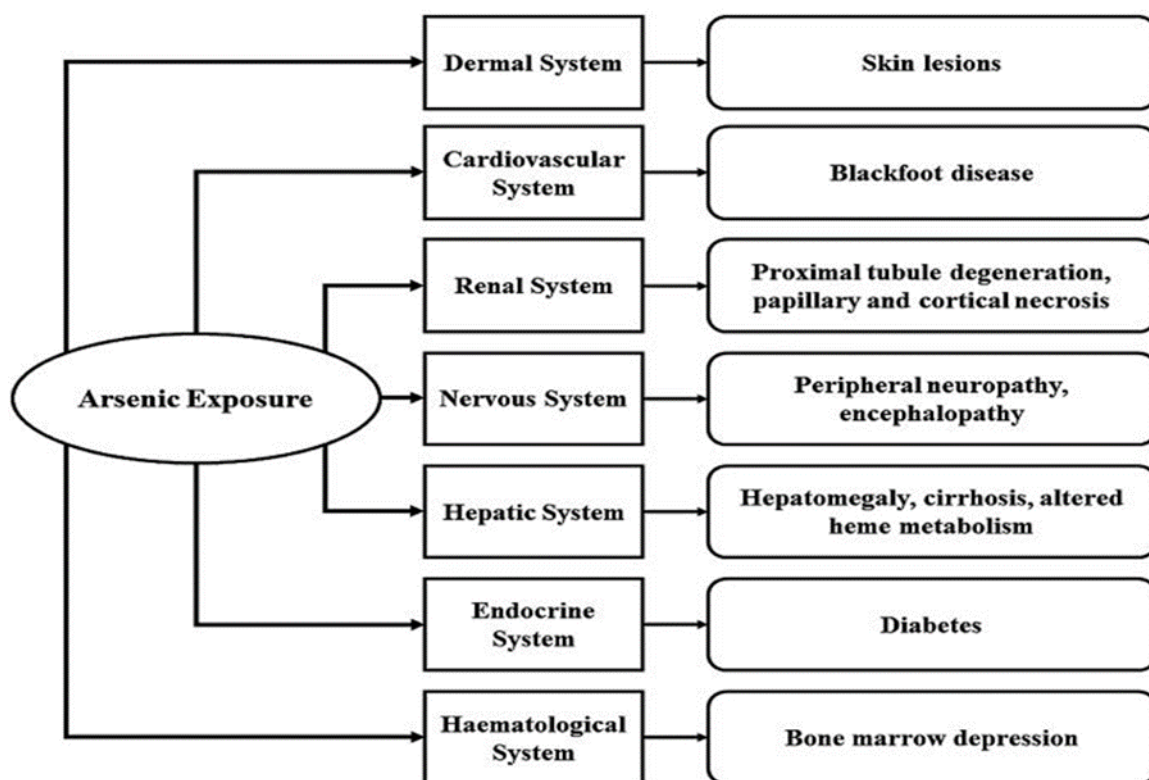


Figure 16. Arsenic exposure effects on major organ systems. (Abdul et al., 2015).

of mercury has risen in recent times, prompting increased research into mercury transport via water. Ha et al. (2017) offers a comprehensive collection of studies focusing on the human health effects of mercury conducted over the past decade that can provide further answers concerning the health effects of mercury.

The extent of arsenic transport within PM₁₀ dust particles and their estimated dosages by area has been studied by Kim et al. (2014) extensively within the Western Mojave Desert. Calico was included within the study area but constituted a minor footnote within the study in favor of larger arsenic-bearing gold mines located north of Edwards Air Force Base. Particulate size of arsenic-bearing dust estimated concentrations within human lung fluid, cancer-related health risks, and non-cancer-related health risks were analyzed by each area within the study site. The study concluded that an increase of one cancer victim per one million would occur in an area affected by arsenic-bearing airborne dust within the Western Mojave Desert.

CHAPTER TWO: METHODS

Study Area

The Garfield Mill site study area is situated 15.1 km (9.4 mi) northeast of Barstow and 5.5 km (3.4 mi) north of Yermo/Daggett, California. It is just 0.5 km (0.3 mi) south of San Bernardino County's Calico Ghost Town Regional Park, and 2.8 km (1.7 mi) north of U.S. Interstate 15 (Figure 1). The study area lies in the heart of the Mojave Desert and within the Mojave watershed. Vegetation is minimal, with small thorny shrubs, cacti, and patches of scattered yucca trees and century plants (*Agave americana*) constituting most of the vegetation. The only animal life observed at the site were occasional birds, probably turkey vultures, and small white to tan lizards of an unknown species. The general weather conditions at the site are typical of desert biomes, with high daytime temperatures in summer, low nighttime temperatures in winter, and very low precipitation and humidity. Seasonal high westerly winds may produce sporadic small haboobs.

Access to the study area was granted by the two jurisdictions governing the site. San Bernardino County granted access to the mill site and upper tailings area, while Dr. Sterling White at the Bureau of Land Management approved field studies in the lower mill tailings area that would not disturb the site with digging. Personal vehicles were used to access the site, while field sampling and data collection were conducted on foot.

Local landmarks include the town of Calico 0.5 km north of the site, currently a regional park with heavy tourist traffic. The Calico Mountains, roughly 0.8 km (0.5 mi) north of the site, are home to the various mines that were the primary sources of silver ore during the district's mining period. The town of Yermo/Daggett lies 5 km to the south, and Interstate 15 is 2.8 km (1.7 mi) south. The Garfield Mill site is located north of the study site just across Ghost Town Road and is easily seen beneath older train trusses used to transport ore down to the mill (Figure 2). Rural residential properties were located at the southernmost tip of the site starting 0.3 km (0.1 mi) west of the Behemoth Mound, which stands nearly 6 m (18 ft) high at its highest point and covers a 0.3 km by 0.2 km (0.1 mi) area. A large, probably Miocene-age dry lakebed lying 1.5 km (0.9 mi) south of the site often creates previously mentioned haboobs on windy days.

Field Methods

Fieldwork consisted of multiple trips to Calico to generate a high-resolution base map, amass geochemical data, and collect tailings and mineral samples. The first trip was a site overview for planning purposes, and to gain familiarity with the area before any data scans or drone photos were taken. An iPad with the FieldMove Clino™ software application was used to supplement notepads, cameras, GPS devices, and laptops. GPS-referenced photos were taken using the app, while area boundaries and locations of interest were noted. General notes were taken for use on future outings and as noteworthy observations that could be useful during data collection.

After scheduling was completed, Dr. Kerry Cato, an engineering geology professor at CSUSB and licensed drone operator, accompanied the second outing to take aerial drone photos of the site. The drone used was a DJI Mavic Pro™ equipped with a high-resolution camera. Each of the batteries brought along allowed roughly 15 minutes of flight (for future outings it's best to bring more than a minimum number, since increased temperatures can shorten the operating time of each battery by almost one-third). This rule should also be considered for any iPad, iPhone, and other device used in conjunction with the drone software, since high temperatures caused the iPad to enter Sleep mode until its temperature fell. This limitation necessitated repeated switching between smart phone and tablet because temperatures sometimes exceeded 110°F.

An aircraft flying below the maximum legal altitude limit of 300 ft, with an average operating altitude of 270 ft, took 436 georeferenced photos for complete site coverage. The point of origin for each flight was at Foundation 1, the northernmost foundation in Sector 1 (Figure 17), allowing even and complete coverage of the site. The drone photos were compiled upon return to CSUSB, then transferred to Agisoft Photoscan. These photos were used to create a high-resolution 3D orthomosaic map (Figure 18) and DEM (Figure 19) of the site. The resulting 3D site map was uploaded to Google Earth™, FieldMove, and Rockworks 17 software for field mapping. Google Earth is used to position the maps within a regional context, for pre-field planning, and as a medium for presenting the data collected.

Geochemical Instrumentation and Software

Data was collected after initial site maps were completed, and scanning excursions were conducted as scheduling allowed. The levels of elements of interest (EOI's), e.g., arsenic and mercury, were measured directly in the field using a Niton XL3t GoldD⁺ portable XRF instrument. Data collected is linked automatically with an onboard GPS to produce georeferenced geochemical data that can be directly downloaded to mapping software such as FieldMove. The instrument was calibrated to a 3-minute scanning cycle, with each scanning segment set to 60 seconds, 30 seconds, and 90 seconds, respectively. These scan times were chosen to maximize detection of EOI's, including Hg, As, Ag, Ba, Cu, Pb, and S. The instrument was linked to GPS during system checks at the beginning of each outing preceding calibration scans. A minimum of three calibrated field standards for mercury and arsenic were analyzed before each field sampling session to assure instrument accuracy. If needed, a linear correction aligned instrument values with calibration values. Detection limits for mercury and arsenic with the portable XRF are ± 6 and ± 4 ppm, respectively, with other elements having a detection limit of ± 10 ppm (Thermo Scientific, 2013). A second backup battery was also brought because high temperatures shortened battery life unpredictably. Depending on the temperature, a single battery could last nearly 6 hours of near-constant scanning or approximately half that on hotter days.



Figure 17. Aerial view of Garfield Mill site tailings, Sectors 1 through 3. Red circles indicate the location of concrete foundations that once supported cyanide leaching operations south of the Garfield Mill (Google Earth, 2019).



Figure 18. Orthomosaic map of Garfield Mill site tailings.

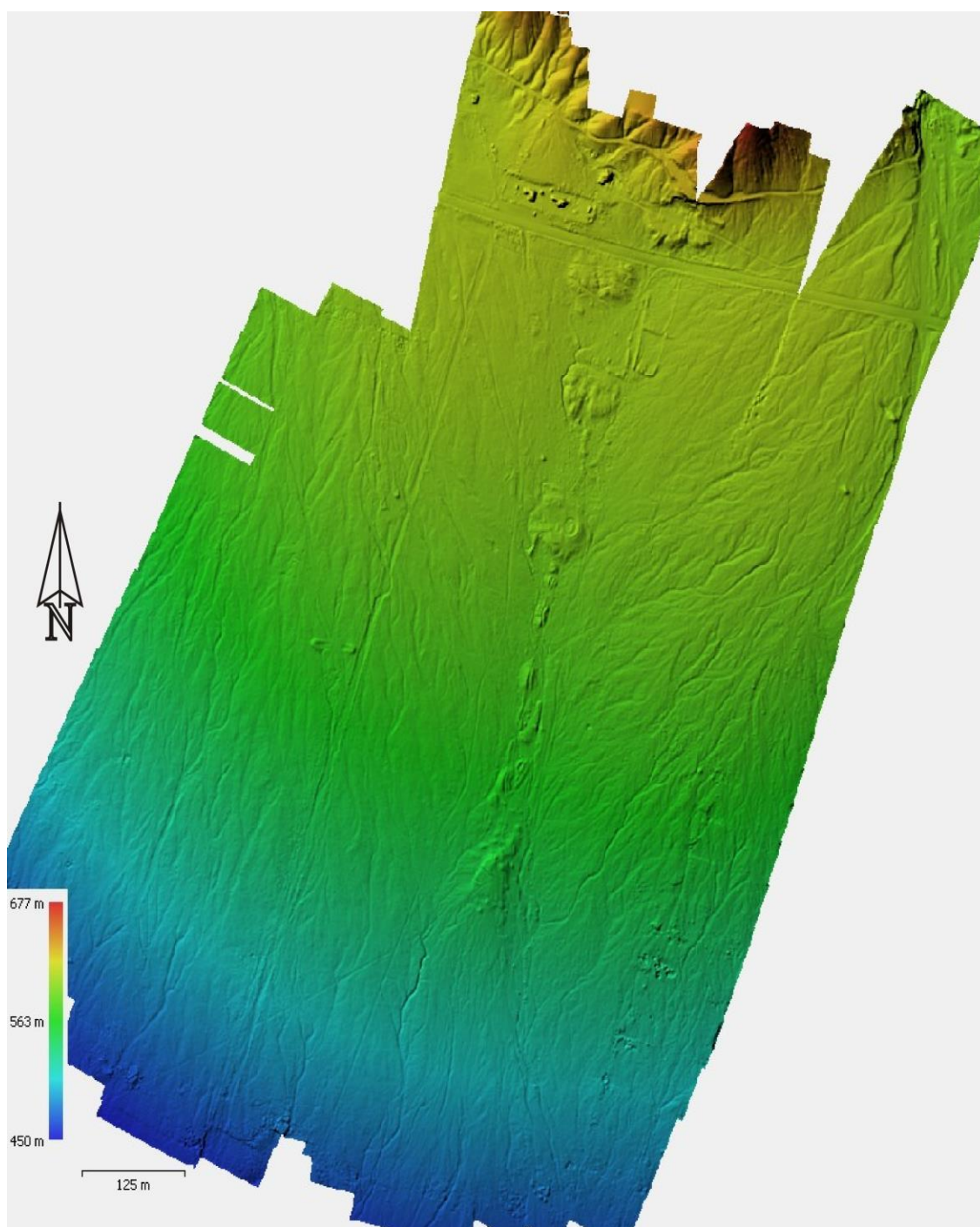


Figure 19. DEM of the Garfield Mill site.

Sampling density was determined by field conditions, with 5 m (16 ft) between samples used for the first coverage interval. When site coverage was complete, secondary coverage was conducted at 3 m (9 ft) sample spacing to achieve greater sampling density and obtain data from areas previously missed.

Tertiary coverage undertaken both during and after secondary coverage identified areas of heightened EOI concentrations; data was collected at 1.5 m (5 ft) interval spacing to achieve highly detailed concentration readings at such hotspots. The site was partitioned into four sectors to aid in future identification of subject piles as well as to aid in the analysis and later discussion of specific areas within the site (Figure 20A). Boundary conditions created to aid the processing of future maps were achieved via a boundary line of scans taken on the outermost perimeter of the site, identified in Figure 20B by a red line. An average of 50 to 60 scans were taken on every outing, with each trip starting at 7 a.m. and ending around noon, although field conditions and scheduling introduced variations. A total sampling of 800 data points was considered the maximum amount required.

Periodic rainstorms and colder temperatures were common during tertiary coverage. Niton scans were not taken during precipitation events because of the potential for instrument damage, and the fact that soil moisture would compromise instrument accuracy. However, data collected following precipitation was inspected to ensure accuracy. Several previously scanned areas were rescanned to determine accuracy; subsequent data analysis confirmed ± 10 ppm difference in samples. Direct sampling of soil was conducted via sterile sample



Figure 20A. Overview of Garfield Mill tailings site. The site has been divided into four sectors for easier description (Google Earth, 2018).



Figure 20B. Aerial overview of tailings site. Red borders indicate extent of geochemical analysis coverage and site area (Google Earth, 2018).

bags brought back to CSUSB for laboratory calibration study using the benchtop Niton FXL XRF analyzer. This instrument, operating in soils mode with sample spinner and helium gas flow, produced much more accurate analyses (± 2 ppm) of individual elements (Thermo Scientific, 2013) to confirm the accuracy of field measurement. While there will be limitations to accuracy with in-situ field measurements, they have the advantage of not requiring disturbance of the potentially toxic tailings material, or disposal of the materials upon return to campus.

Following benchtop Niton scans, XRD then prepared samples for analysis to determine mineral composition and identification. The samples were ground using an automatic rock grinder, which was then rinsed, cleaned, and exposed to compressed air to ensure that no leftover moisture would compromise the XRD samples. The seven samples were then processed via the Geology Department's XRD analyzer after instructions on proper operating procedure were provided by Dr. Codi Lazar, a geochemistry professor at CSUSB. Each sample went through a 90-minute analysis. Upon completion, the readings were corrected and correlated to the minerals most likely to be found within the samples (Figures 21 and 22). Special attention was given to mercury- and arsenic-bearing minerals to determine elemental mineral speciation for pre/post-milling comparison, which will be discussed in Chapter Three.

Field samples from Calico were examined under a Phenom XL SEM operating at 10 kV for images and 15 kV for element analysis. Samples for SEM analysis were prepared by gravity concentration and magnetic separation, then

mounted on a 5-mm aluminum sample post using double-sided carbon tape. SEM samples were then analyzed for element content and images were produced for use in figures.

CHAPTER THREE: RESULTS

Mineralogy and Chemistry of the Tailings

Tailings Mineralogy

XRD detected rich sulfides of lead and iron (galena, PbS and pyrite) within the Garfield Mill tailings, while black, highly oxidized sulfides were also found; these proved to be manganese-rich sulfides in the form of alabandite (MnS). Although they were not specifically documented in earlier works, EOI's such as arsenopyrite (Fe–As–S), realgar (As–S), and proustite ($\text{Ag}_3\text{As–S}_3$) were searched for during XRD analysis of collected soil samples to understand whether they were present before or after the milling process (Figures 21 and 22). Arsenopyrite and realgar (As_4S_4) were found to be the most common minerals of arsenic within the tailings, appearing in all but soil sample 7, which was sourced from the Behemoth Mound. In addition to these metalliferous minerals, most of the tailings consisted of a mixture of barite and sanadine.

The presence of arsenic trioxide (claudetite) was tested for in addition to other compounds, since it is the primary product of arsenic-bearing mineral combustion (Chakraborti, 2015). It was found within the Garfield Mill tailings in the form of the mineral claudetite (AsO_3). XRD identified well-defined layers of yellow material in the tailings as claudetite and other oxidation products of naturally occurring arsenopyrite (FeAsS). Yellow layers were typically overlain by

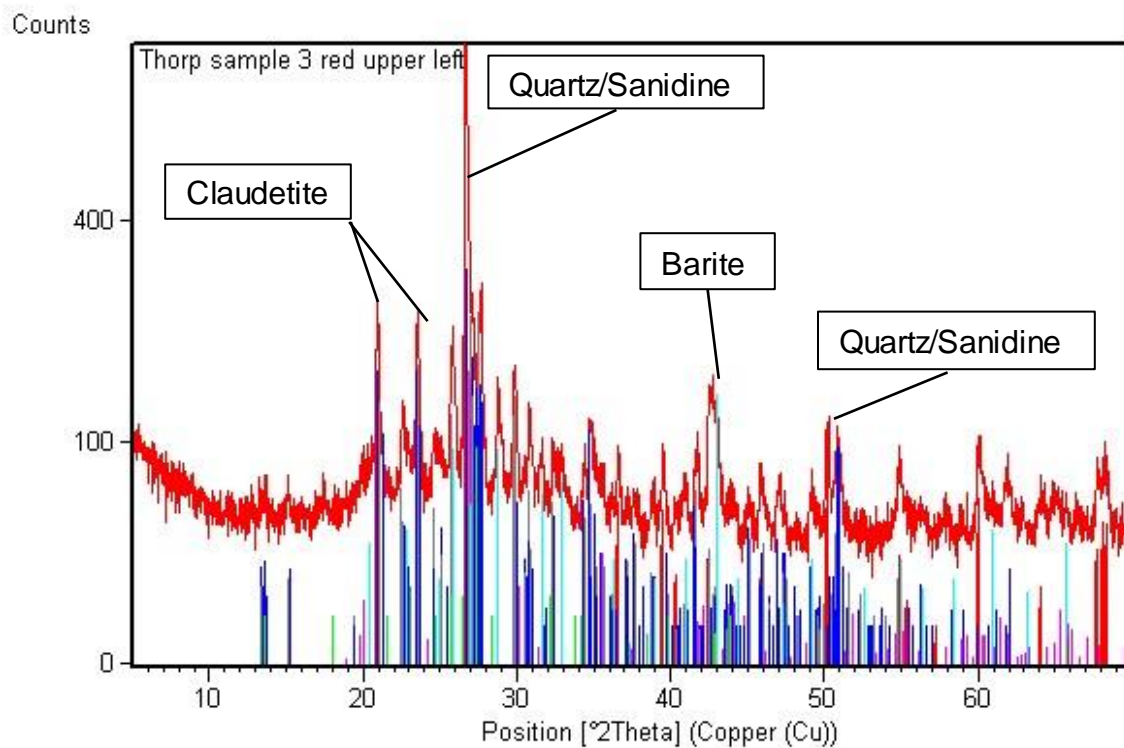


Figure 21. XRD chart of sample 3 from the Garfield Mill site tailings. Sourced from Sector 1, pile 3.

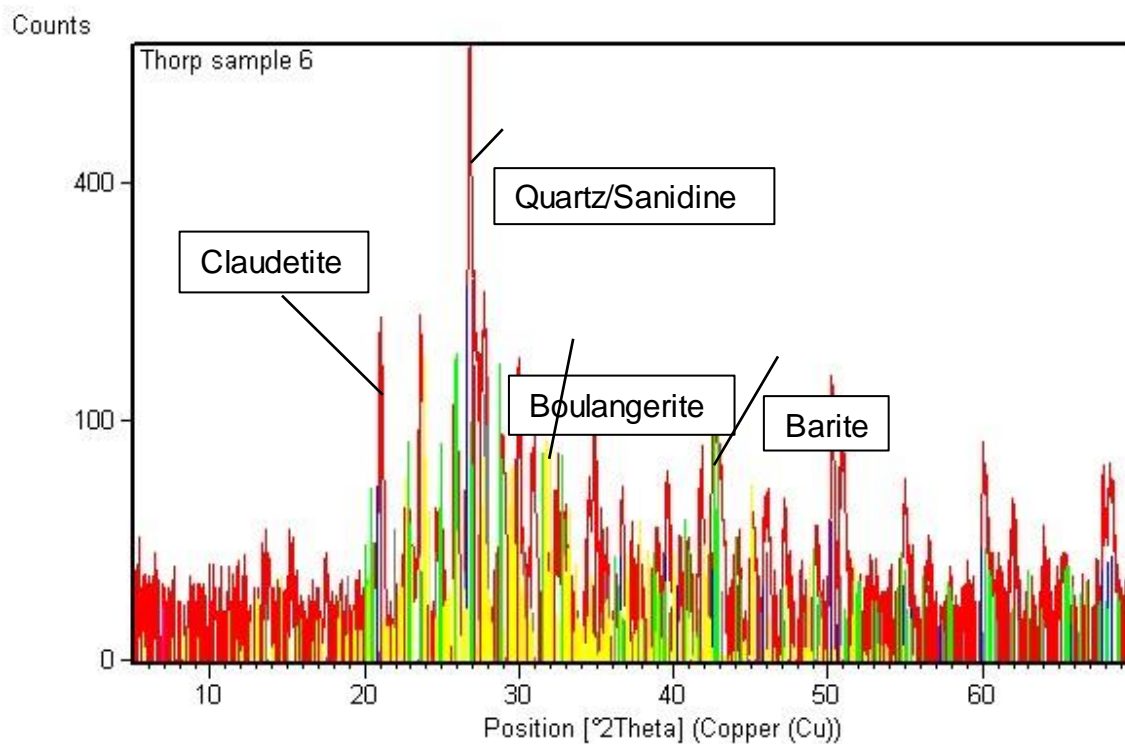


Figure 22. XRD chart of sample 6 from the Garfield Mill site tailings. Sample was sourced from Sector 3, pile 3.

layers of sanidine, barite minerals, and occasional potassium-rich silicate minerals.

The heightened presence of mercury at Calico both during and after the district's mining period have been confirmed both from field data and from historical sources describing the way locals would often "mine" the sands and cement foundations of the old mill sites for mercury after they had closed (Lane, 1993). XRD did not detect native elemental mercury, nor mercury-bearing compounds. Traces of silver halide minerals were found in the tailings, but at very low levels. Lead was found in moderate concentrations (1,500–2,000 ppm) throughout the Garfield Mill tailings site, occurring as galena in most areas, while trace readings of vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) were found within Sectors 3 and 4.

Although arsenic and mercury were detected using XRF, and some arsenic compounds were detected using XRD, SEM analysis of field samples detected few toxic elements. Of the SEM samples analyzed, none was observed to be magnetic. Granules of quartz (SiO_2), barite (BaSO_4), Fe–Ti oxides such as ilmenite (Fe_2TiO_3), sanidine ($\text{K(AlSi}_3\text{O}_8)$), various salts (mostly KCl), and chrysocolla ($\text{Cu}_{2-x}\text{Al}_x(\text{H}_2-x\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$) made up the majority of the sample granules, while exceptionally small sample grains (<10 nm) that contained Pb, As, S, and Sb were also found (Figure 23). This mineral assemblage will be discussed later, but because of the hydrothermal formation conditions at Calico, it is possibly two minerals formed as a result of the weathering of other rocks such as realgar and bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_6\text{O}$) that resulted in minerals such as orpiment (As_2S_3). The latter two minerals were the

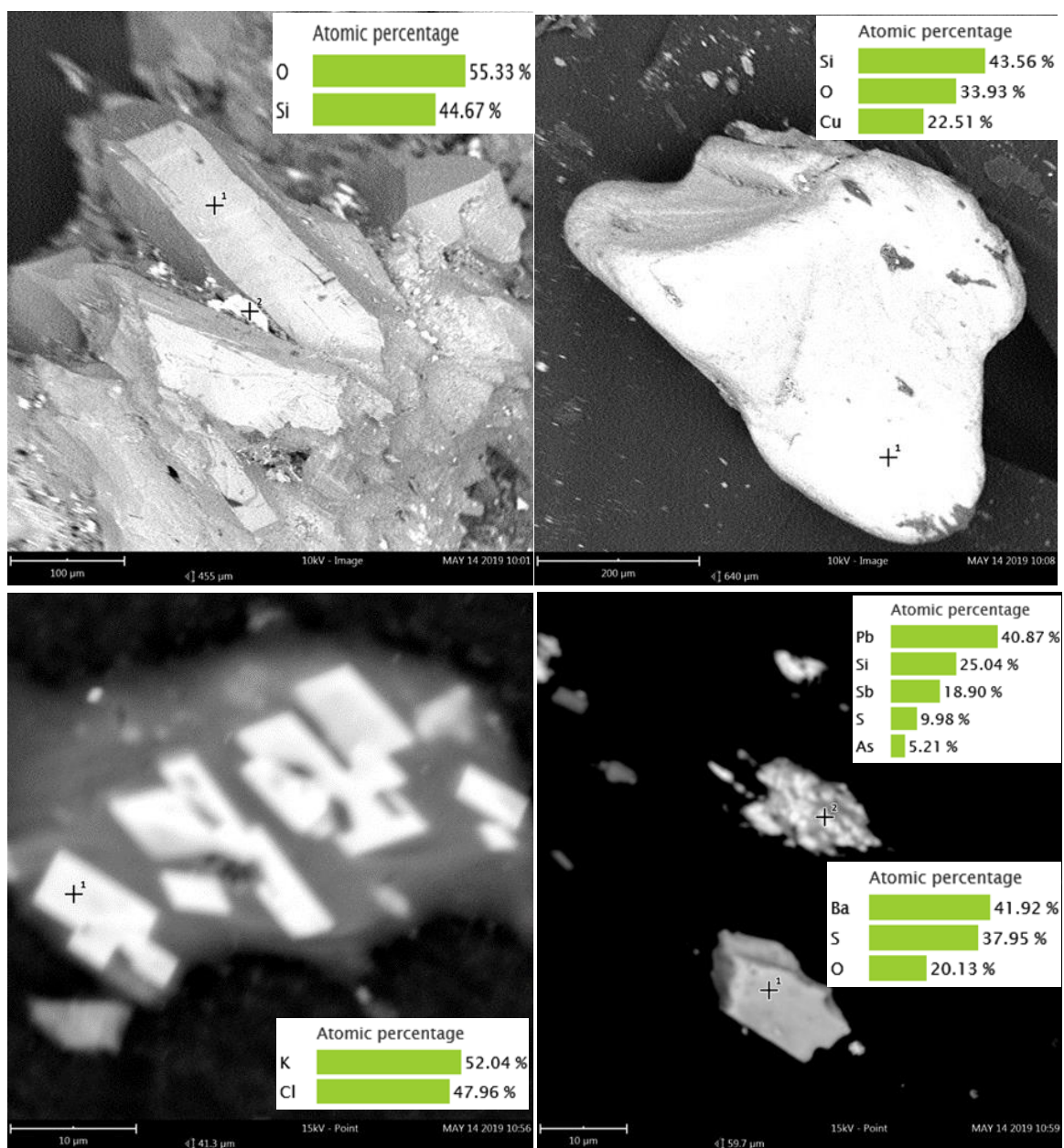


Figure 23. SEM images of sample grains from the Garfield Mill site. Images show quartz (upper left), chrysocolla (upper right), KCl salt (lower left), Sb–Pb compound with intrusions of quartz and orpiment/realgar (lower right, upper grain), and barite (lower right, lower grain).

only ones found containing As, and no Hg-bearing compounds were found using SEM.

Tailings Chemistry

The EOI's in the Garfield Mill tailings were found to have a wide range of values. Silver was one of the most interesting results. Silver values within the tailings ranged from a low of 5.43 ppm (0.18 opt) to a high of a staggering 411 ppm (13.21 opt), with an average of 95.1 ppm (3.06 opt). Barium represents a significant amount of the mill tailings, with a low of 991 ppm, a high of 127,182 ppm (12.7 wt.%), with an average of 35,356 ppm (3.5 wt.%). Base metals were also generally elevated, with Pb having a low of 18.4 ppm, a high of 6,304.2 ppm, and an average of 542.93 ppm. Cu exhibited a low of 10.58 ppm, a high of 4,286.9 ppm, and an average concentration of 620.27 ppm. Zn had a low of 40.85 ppm, a high of 1,791.44 ppm, and an average of 252.29 ppm.

Among the most toxic constituents, As ranged from a low of 9.45 ppm to a high of 1,800 ppm, averaging 141.3 ppm throughout the site. Sector 1 contained both the widest distribution and the greatest concentrations of As. Hg concentrations were a low of 4.23 ppm, a high of 664.12 ppm, and an average of 36.75 ppm. XRF scanning of the cement foundation of the former mill site often measured elevated mercury concentrations in excess of 250–300 ppm. Foundations located within Sectors 3 and 4, believed to have been part of the cyanide leaching plant, also contained heightened Hg concentrations.

Tailings Maps and Volumetric Estimation

Geochemical Distribution and Concentration Maps

Chemical distribution maps of the Garfield Mill site EOI's include lead, silver, arsenic, mercury, and copper (Figures 24 through 28). Silver distribution was the most variable among EOI's, with the majority found in piles 1, 3, and 4 of Sector 1. These piles were located along the perimeter of the mill site and the primary mill tailings dump (Figure 27A). While efficiencies estimated to be 85–90% were achieved at the mill silver loss was economically and mechanically inevitable, which meant that the tailings closest to the mill were richer in silver than the rest of the tailings, reaching concentrations of as much as 425 ppm. Silver concentrations averaged around 250–300 ppm throughout the entirety of the Garfield Mill site (Figure 24), with many areas exhibiting heightened concentrations exceeding 325 ppm. Pockets of silver were also located in Sector 2, while notable concentrations of 300–375 ppm appeared throughout Sector 3 from piles 1 and 3. Sector 4, which accounts for the Behemoth Mound, curiously saw a pocket of silver concentrations reaching up to 325 ppm that stopped abruptly at the borders of the Behemoth Mound. This was not a tailings pile but the concrete foundation of some facet of the mill site, so the silver had probably spilled along with the mercury amalgam and had been deposited into the cracks in the foundation which had been subsequently weathered by wind, rain, and abrasion for more than a century since the mill's operation (Figure 13).

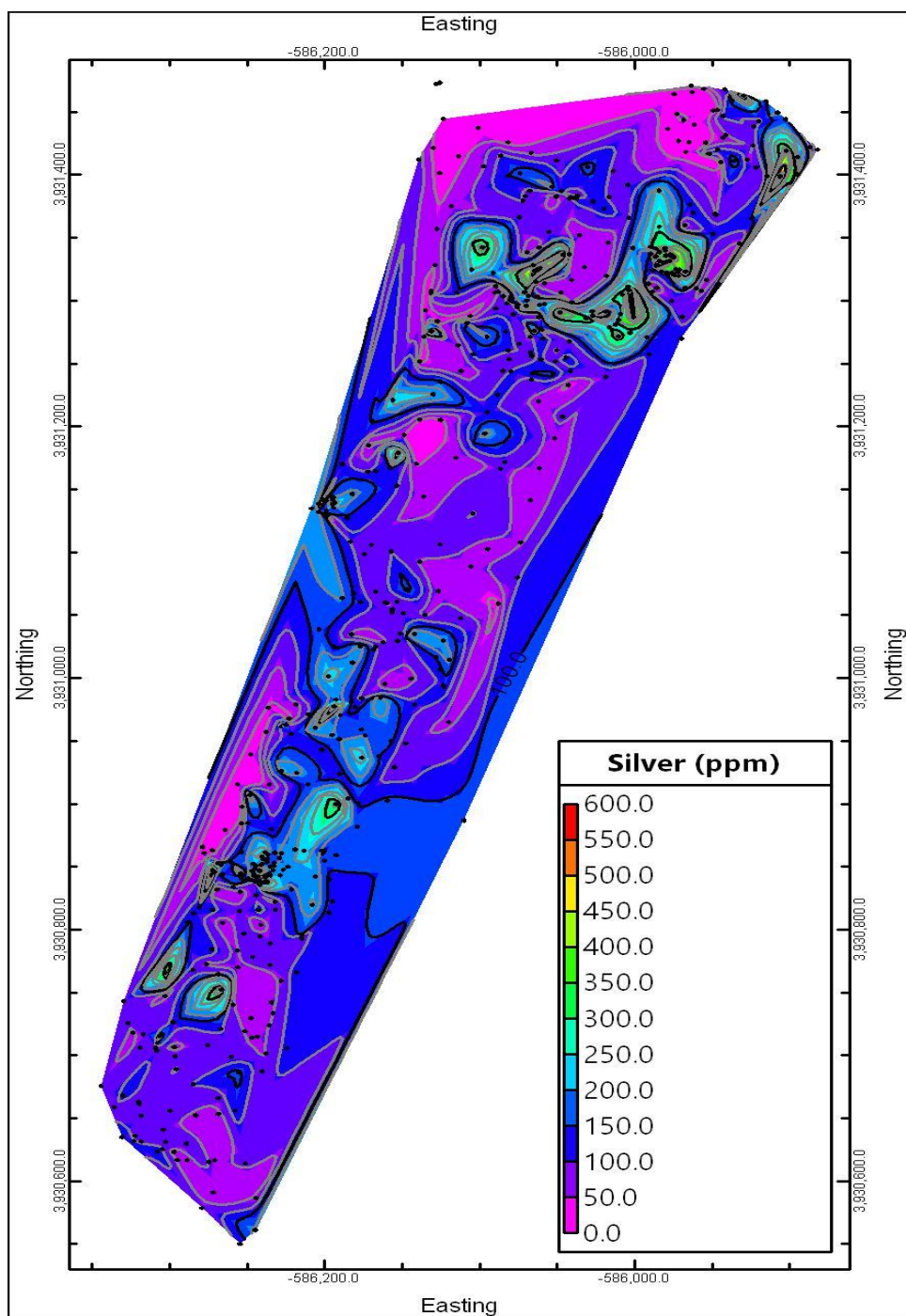


Figure 24. Ag distribution at the Garfield Mill site.

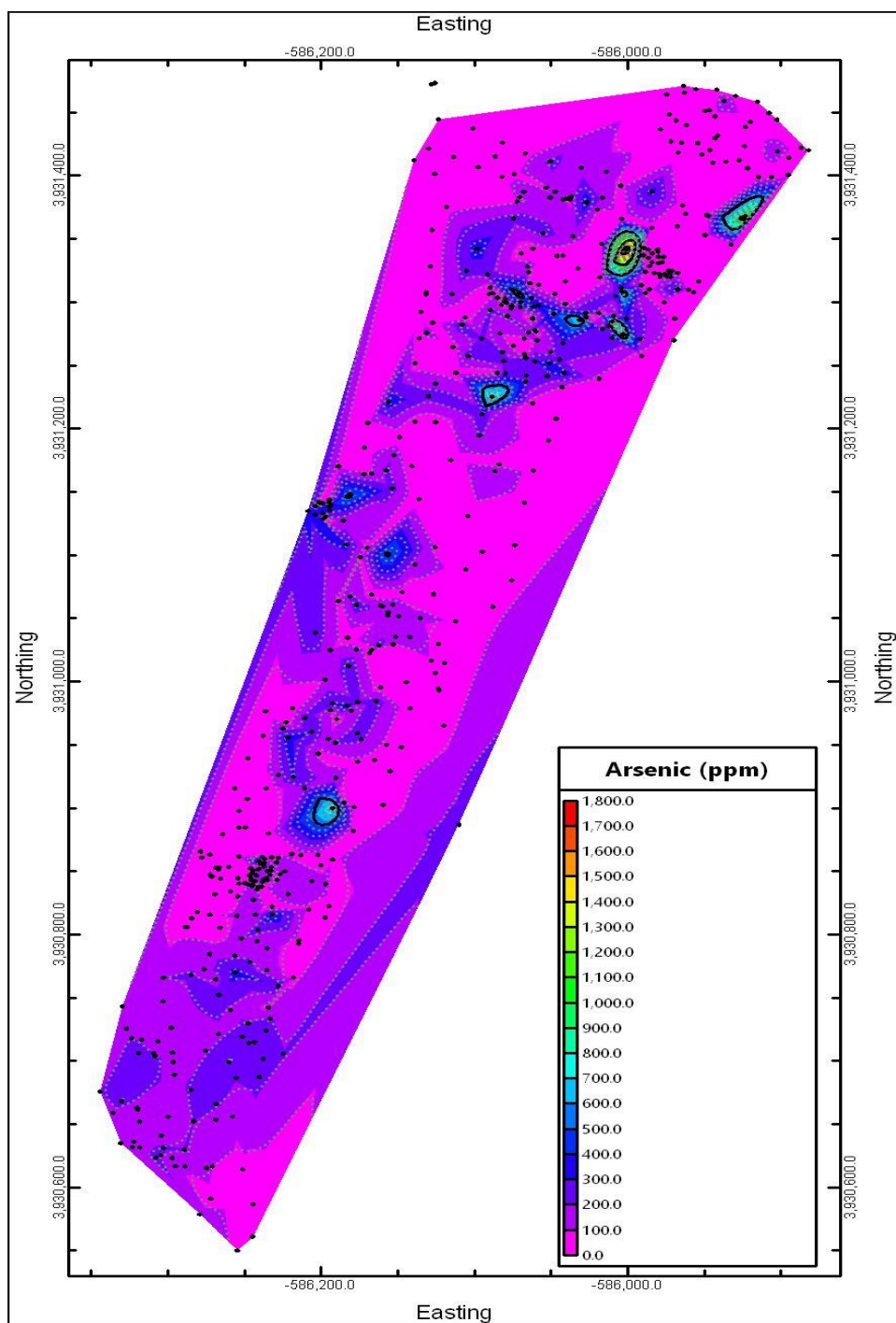


Figure 25. As distribution at the Garfield Mill site.

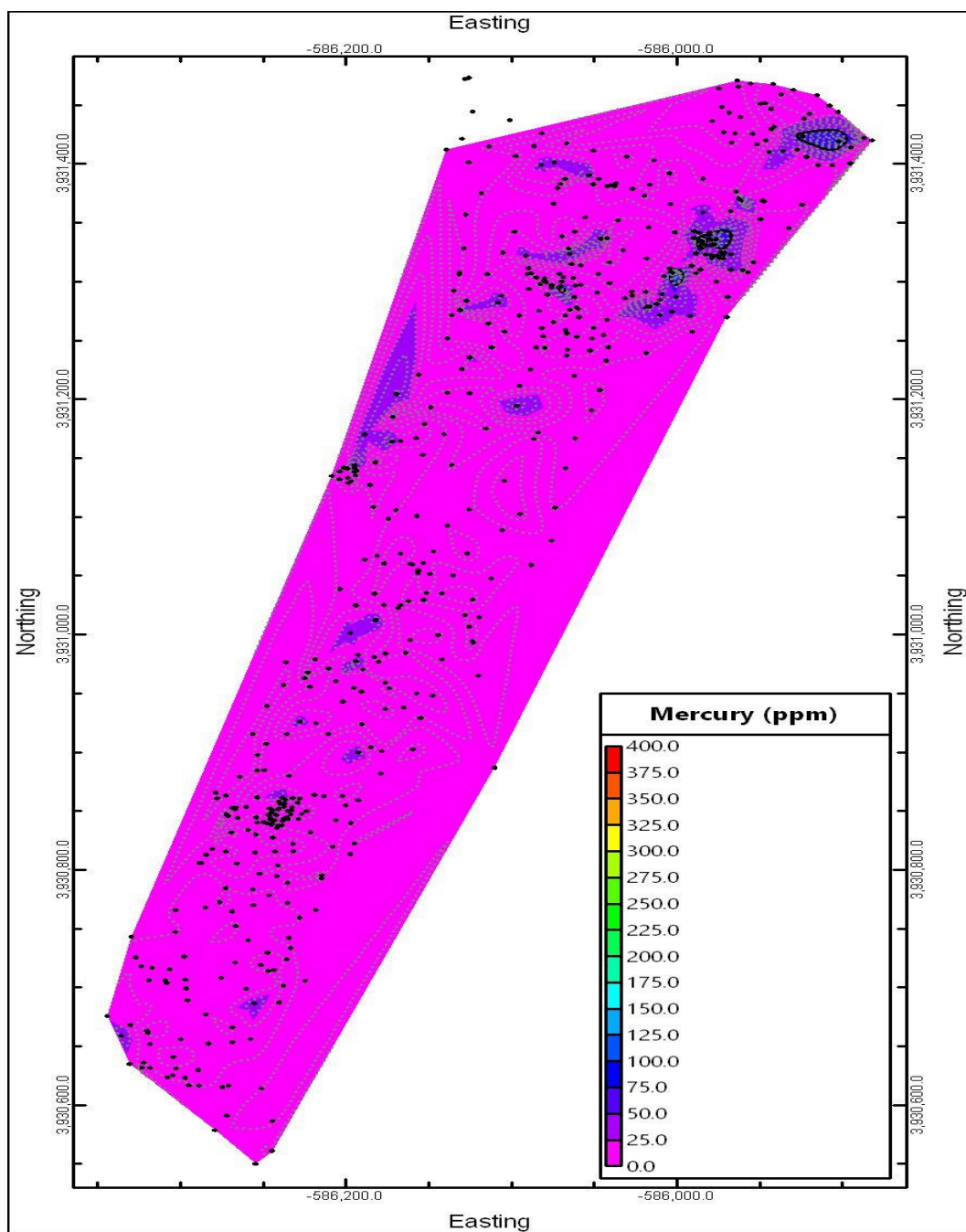


Figure 26. Hg distribution at the Garfield Mill site.

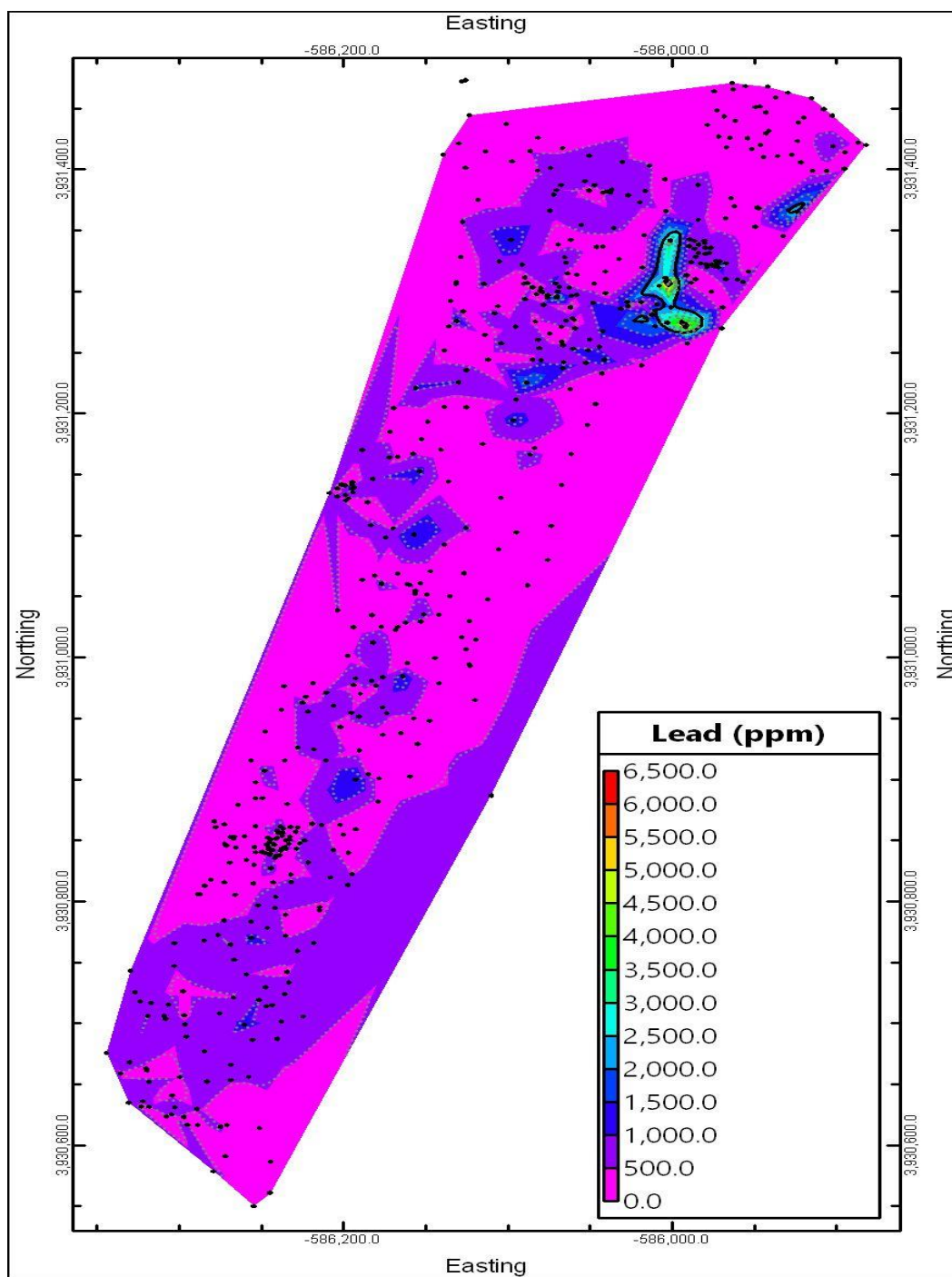


Figure 27. Pb distribution at the Garfield Mill site.

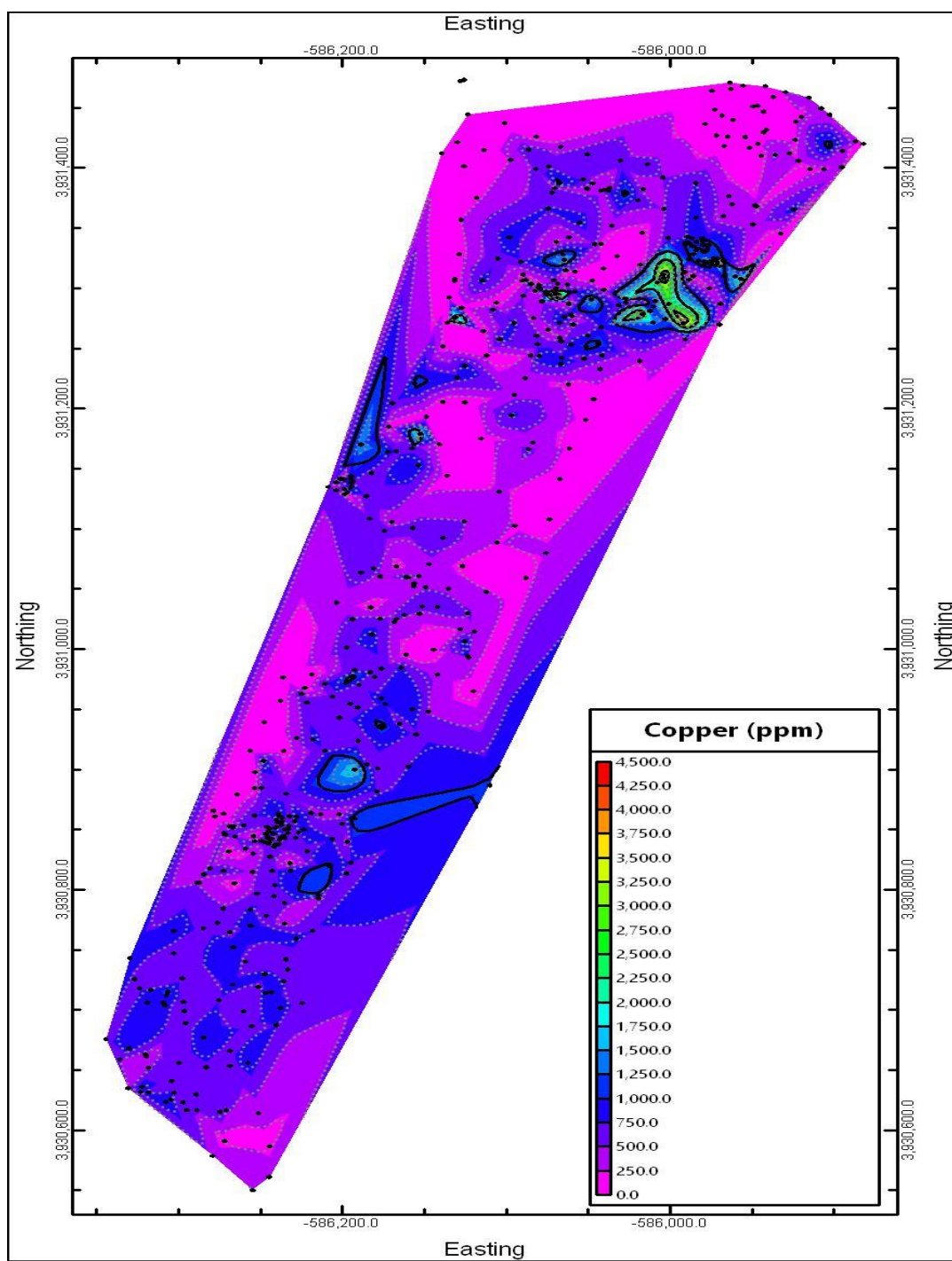


Figure 28. Cu distribution at the Garfield Mill site.

Silver concentration usually increased together with the heightened presence of mercury and arsenic, but controversially, concentrations would drop to ≤ 175 ppm in the presence of very high concentrations of arsenic (over 1,000 ppm) and lead (over 3,000 ppm).

Arsenic was primarily distributed within piles 1, 3, 4, and 5 of Sector 1 (Figure 29A), with additional concentrations at pile 2 of Sector 3 (Figure 29C). The greatest concentrations of arsenic found were 1,800 ppm at piles 1 and 3 of Sector 1, while all other hotspot readings reached 1,400–1,500 ppm at most (Figure 25). Elevated arsenic levels exceeding 600 ppm were found throughout the site's entirety, even in locations along the site's borders that appeared to have no visible tailings. High concentrations of arsenic in Sector 1 coincide with the chemical distributions of silver and mercury, since increased arsenic content caused increased mercury and silver loss in the tailings. Nonetheless, the heightened levels found throughout the site were far higher than originally expected, while the "hotspots" within Sector 1 were unexpected. Both hotspot locations contained patches of tailings that were a pale, sickly yellow easily distinguished from the normally white to red-tan color of the tailings. This material, tested using laboratory XRD analysis, was identified to be a mixture of arsenopyrite and claudetite that was probably produced through the partial combustion or exposure to steam during the milling process.

Mercury distribution coincided greatly with silver distribution (Figure 26), although the number of hotspots were limited. Sector 1 remained the area with the widest distribution of mercury; it contained the highest concentrations found

at the site, with measurements exceeding 700 ppm found at pile 3. Pile 1 contained concentrations ranging from 200 ppm to 250 ppm but had wider distribution, with the entire pile having heightened levels throughout. Sector 2 contained two large distribution plumes that mirrored pile 1, located at piles 6 and 8. Sectors 3 and 4 had little mercury distribution, but still contained pockets peaking in concentrations of 200 ppm. The weight of the mercury is probably the cause of its limited distribution outside Sector 1, which may also explain the distribution of silver being found primarily in Sector 1 as part of the ejected mercury amalgam.

Lead distribution was the widest, second only to that of silver (Figure 27). Sector 1 had the highest concentrations, with a peak of 6,500 ppm at piles 1, 3, and 4. Sector 1 had the widest distribution of lead, with nearly the entire sector having heightened lead concentration averaging between 1,500 ppm and 2,000 ppm. Sector 2 contained moderate concentrations (1,500–3,200 ppm), with distribution favoring the western side of the sector within pile 1. Sector 3 exhibited similar concentration around its center within pile 1 and at the northern and southern tips of pile 3 and the entirety of pile 1. Sector 4 contained similar Pb concentration throughout its entirety except for the northwestern corner, where concrete foundations were located; the whole of the Behemoth Mound and its surroundings had concentration levels averaging 1,500 ppm.

Copper levels were mapped to establish a possible correlation between its distribution and those of the other EOI's (Figure 28). Distribution mimicked that of

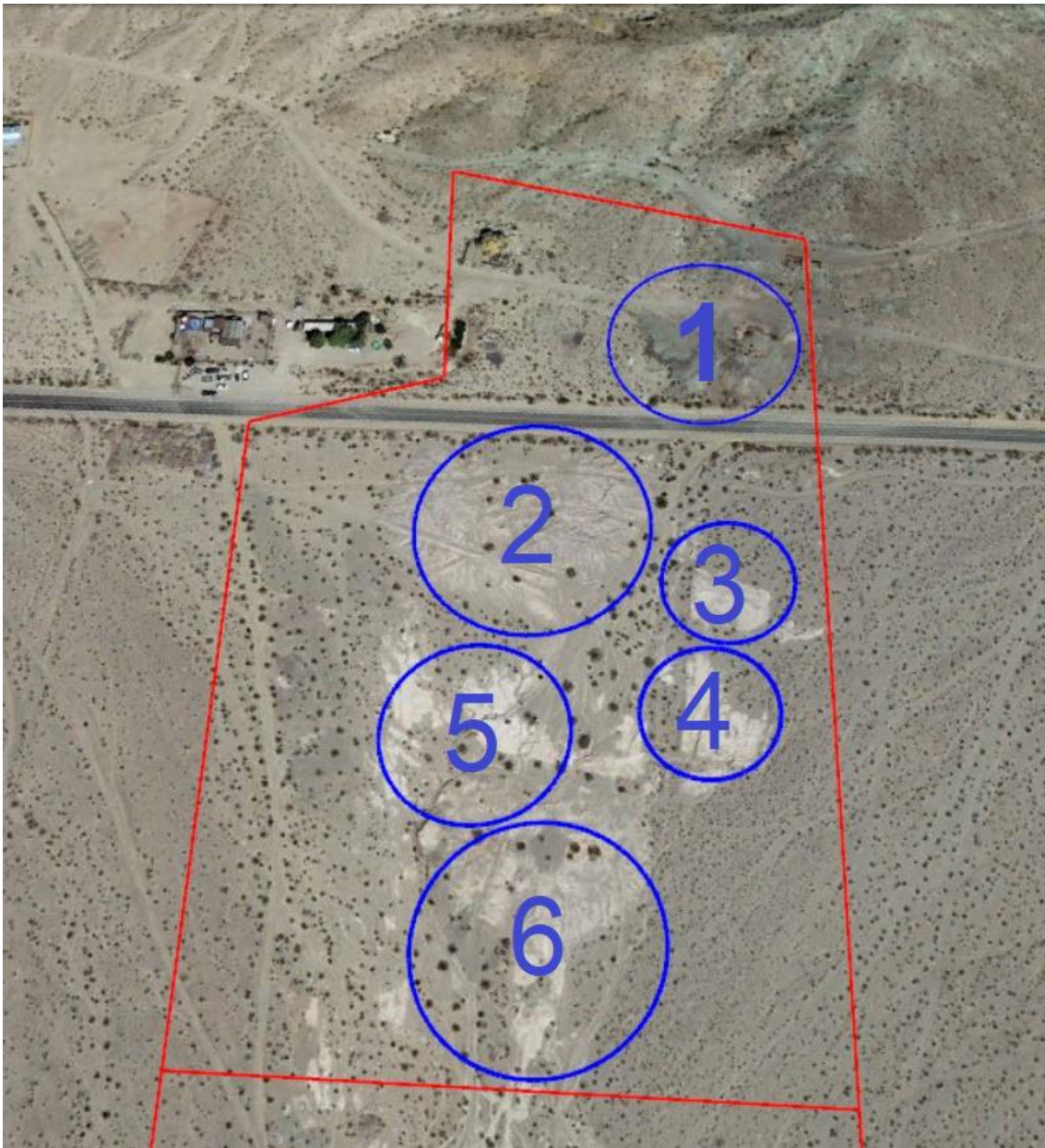


Figure 29A. Sector 1 of Garfield Mill tailings. Blue circles indicate notable tailings piles (Google Earth, 2019).



Figure 29B. Sector 2 of the Garfield Mill tailings. Blue circles indicate notable tailings piles (Google Earth, 2019).

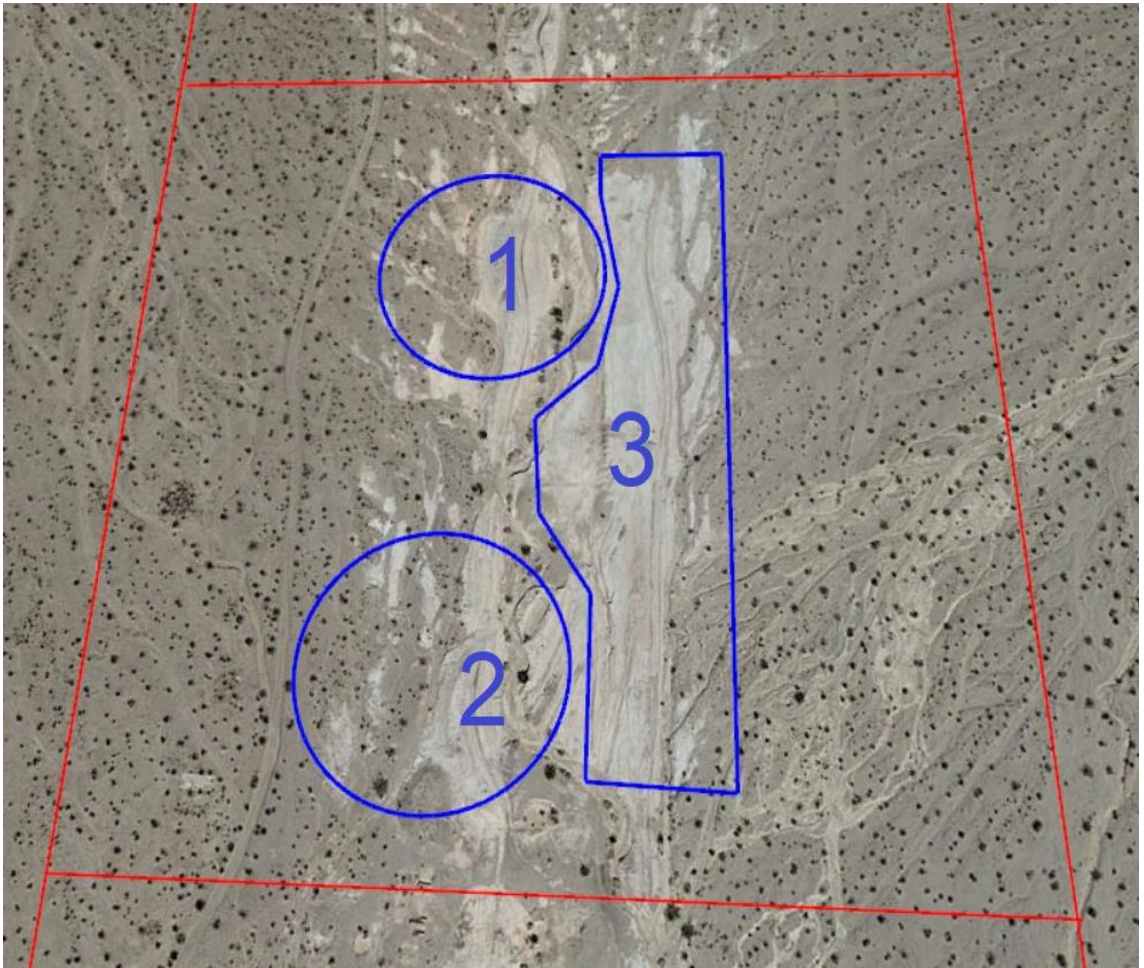


Figure 29C. Sector 3 of the Garfield Mill tailings. Blue circles indicate notable tailings piles (Google Earth, 2019).

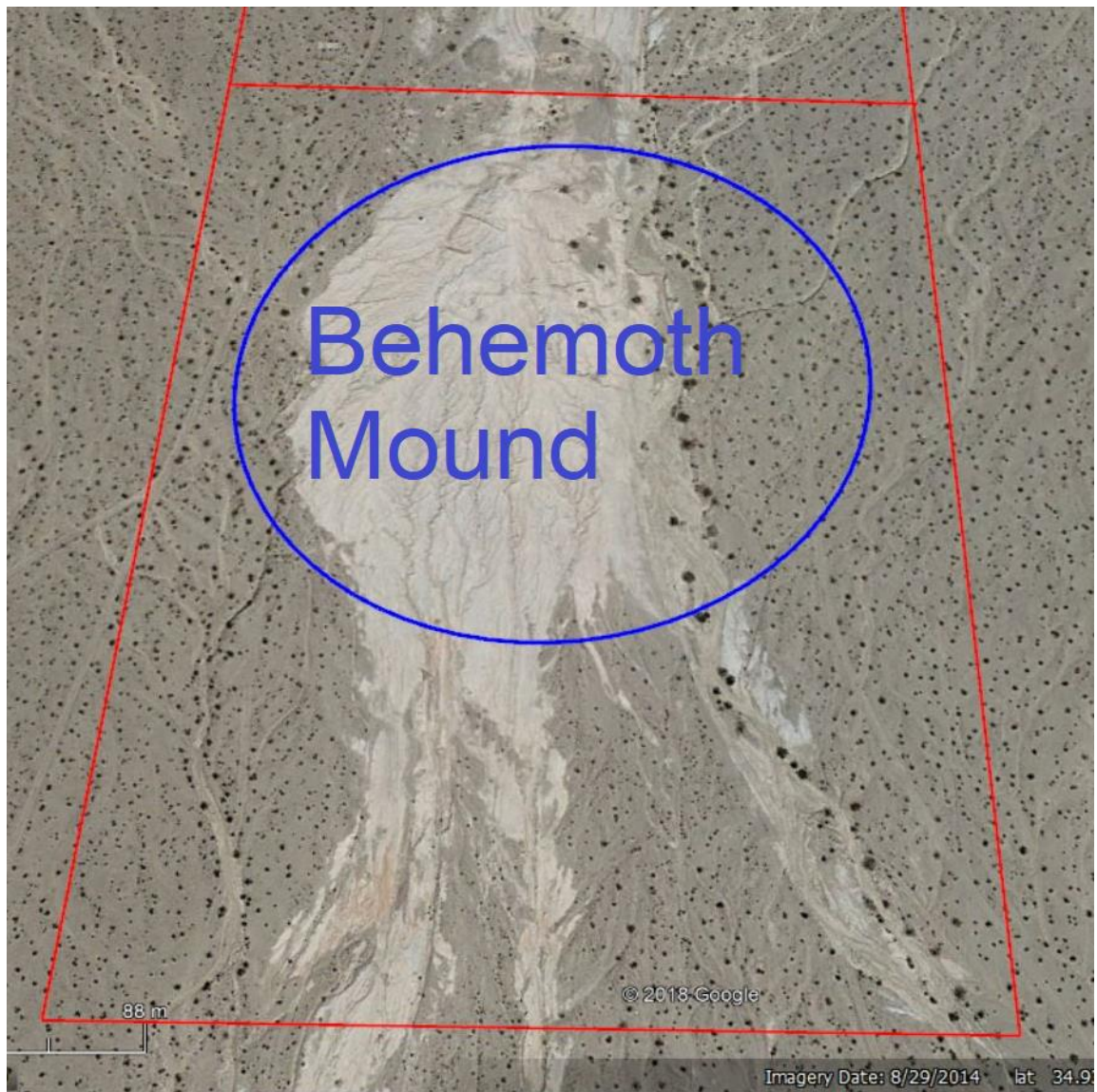


Figure 29D. Sector 4 of the Garfield Mill tailings. Blue circle indicates location of the Behemoth Mound (Google Earth, 2019).

silver, although concentrations were far higher, reaching maximums of 4,500 ppm, hotspots reaching 3,500 ppm, and an average concentration of 1,200–1,500 ppm throughout. Sector 1 had the highest concentration at piles 3 and 4, reaching concentration of 4,500 ppm, with the areas connecting these piles exceeding 2,500 ppm. Outside Sector 1, copper exhibited very wide but relatively low concentrations, ranging from lows of 750 ppm to averages of 1,500 ppm. Sector 2 had a small hotspot near its upper left-hand corner reaching 3,000 ppm, and Sector 3 had no major hotspots but uniform concentrations and distribution. Sector 4 contained one hotspot at pile 1 that reached 2,000 ppm but otherwise had average concentrations and even distribution both within and around the Behemoth Mound.

Aside from the EOI's listed, the distribution of potassium was also investigated owing to the district's use of KCN leaching towards the end of its operational period. Potassium cyanide was the chief leaching solution used during this time, which probably explains the heightened presence of K within the entirety of the tailings. Zn and Ba mapped similarly, with Zn and K mirroring Cu in concentration and distribution, while Ba was present throughout the entirety of the site, as it made up much of the mined ore.

Volumetric Calculations of Mill Tailings

Field measurements of thicknesses of the deposited tailings were made where erosion by rainfall had exposed local bedrock. A total of 273 data points were collected detailing latitude, longitude, and thickness of tailings in meters for

use in generating an isopach map (Figure 30). The volume of the Garfield Mill tailings was estimated in RockWorks17 software using the Delaunay triangulation method. These calculations used a density of 2.215 g/cm^3 , derived by testing the density of several tailings samples collected in the field. The tailings of the Garfield Mill have a volume of 120,992 cubic meters and a mass of approximately 267,998 metric tons. The thickness of the tailings ranged from a few centimeters along the edges of the piles to mounds that attain 4.57 m (13 ft) in height (Figure 30). With the total mass and volume of the Garfield Mill tailings accounted for, the next step was calculating the mass of individual elements to understand the breadth of environmental impact by more toxic elements. RockWorks17 software was also used to generate 2D maps of the distribution of EOIs within the tailings deposit (Figures 24–28). The software generated this 2D map assuming that chemical distribution within the depths of the tailings was uniform, because of the inability to analyze the tailings accurately without drilling equipment, which this study lacked in terms of time, budget, and permissions from governing bodies. The resulting 2D distribution maps for each element give a fair estimation of each element in units of mg/kg.

The RockWorks17 software was then used to combine the isopach map and 2D element distribution maps to produce a volumetrically weighed budget for each EOI. This method was used to estimate the total mass of individual elements throughout the tailings, as it gives more accurate estimates than simply multiplying the mass of the tailings times the average element concentration. These calculations indicate a total of 33.2 metric tons of As, 120.6 metric tons of

Pb, 17.9 metric tons of Ag, 7 metric tons of Hg, 137.1 metric tons of Cu, 8,445.3 metric tons of Ba, and 67.7 metric tons of Zn. The sum of these EOI's was 8,828 metric tons of material, accounting for 0.03% of the total mass of the mill tailings.

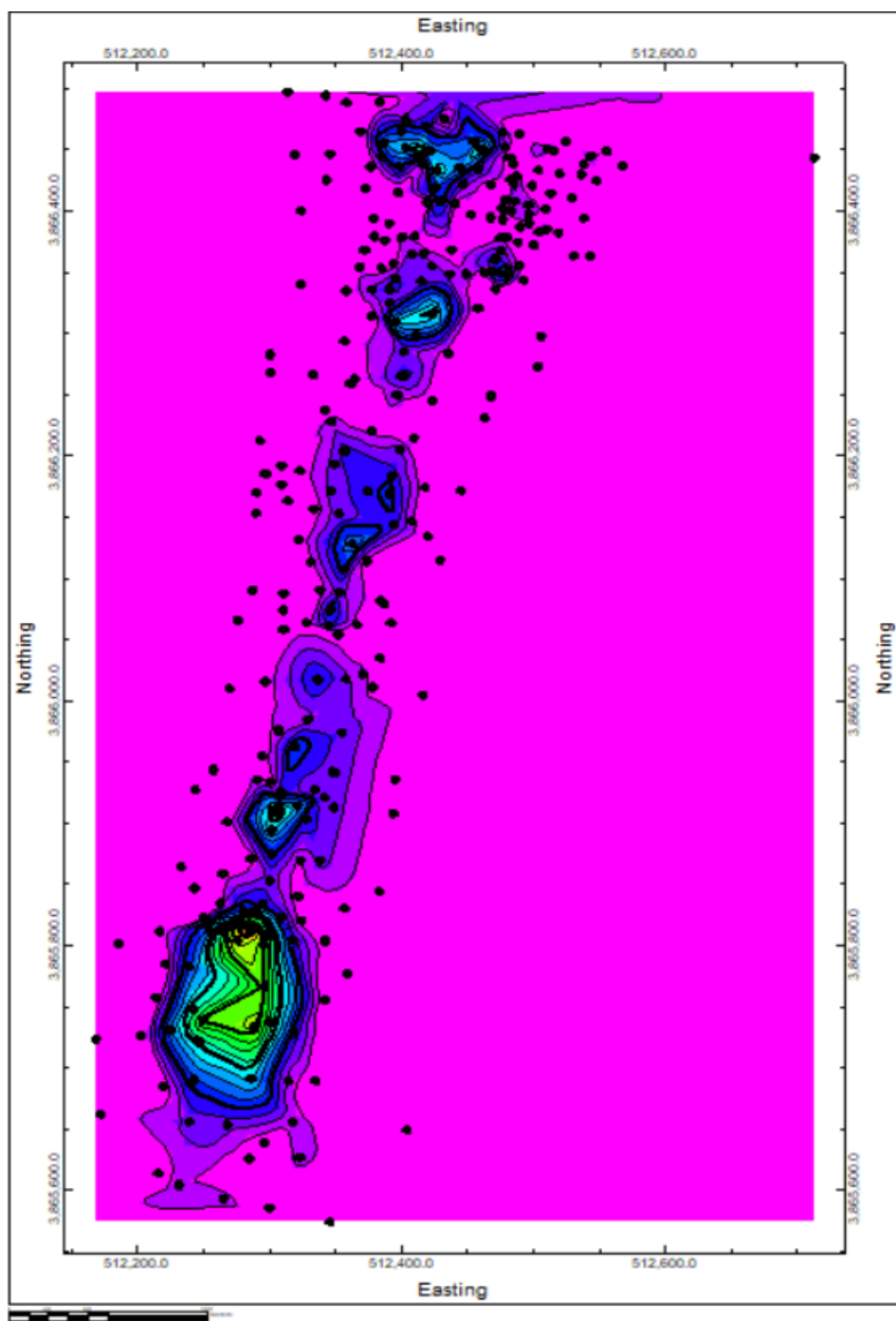


Figure 30. Isopach map of Garfield Mill tailings. Brighter colors indicate higher elevations of tailings.

CHAPTER FOUR: DISCUSSION

Environmental Impacts

Speciation and Stability of the Mill Tailings

The mercury present within the tailings is believed to be foreign to the area, having been brought to Calico for use in the mills. Previous mineralogical reports conducted by Lindgren (1887) and Weber (1966) make no mention of naturally occurring mercury, further validating this notion. It was initially proposed that heavier elements such as lead and mercury would be found in greatest concentrations near the mill site foundation and its immediate perimeter, while others may be distributed more widely owing to lower density or specific chemical interactions. This conjecture was proved to be correct: the distributions of these elements often coincided with one another, in some cases mirroring each other closely. Heightened concentrations of mercury were usually found alongside increased concentrations of silver, as seen clearly in Figure 31. As mentioned in Chapter One, the milling process would lose greater amounts of mercury and silver because of the presence of various elements such as lead and arsenic in the lode rock, so it was theorized that the distribution and concentrations of these EOI's would probably coincide. Such is the case with lead and silver, while XRD sampling has confirmed the presence of arsenopyrite $[(\text{Fe}, \text{Co}) \text{AsS}]$ and realgar (AsS) . Periods of reduced amalgamation efficiency would have immediately followed the mining of veins with heightened amounts of such minerals owing to the reactions they would undergo with the mercury.

Calico's mineralogy has been documented previously by several sources including Lindgren (1887), Weeks (1929), and Weber (1966, 1967). Such studies usually focused on the economic mineralization of the silver ores and less upon the surrounding minerals of lesser economic, but higher environmental, importance. Specifically, many of the former mines have caved in since their closure, while a general lack of economic importance has left some of the finer details of Calico's mineralogy left unstudied. However, examining the mill tailings at the Garfield Mill site confirms that the site contains various arsenic- and lead-bearing minerals in sizeable quantities.

The mineralogy of the tailings is a result of the processing of the parent ores by the Garfield Mill, the physical and chemical weathering of the tailings by aeolian and fluvial factors, cyanidation leaching, then further weathering. Many of the economically important minerals such as silver, barite, and chrysocolla were documented both before and during the operation of the Calico Mining District and later found within the tailings. The presence of minerals bearing arsenic and lead, however, were never elaborated upon in great depth and often overlooked owing to their lack of economic value at the time. No known sources have documented the specific arsenic- and lead-bearing minerals within the Calico Mining District even though the presence, speciation, and effects on the milling process caused by these arsenic-bearing minerals are of great importance to the current state of the mill tailings present at the Garfield Mill site, which show a positive correlation between heightened presence of mercury and increased arsenic levels.

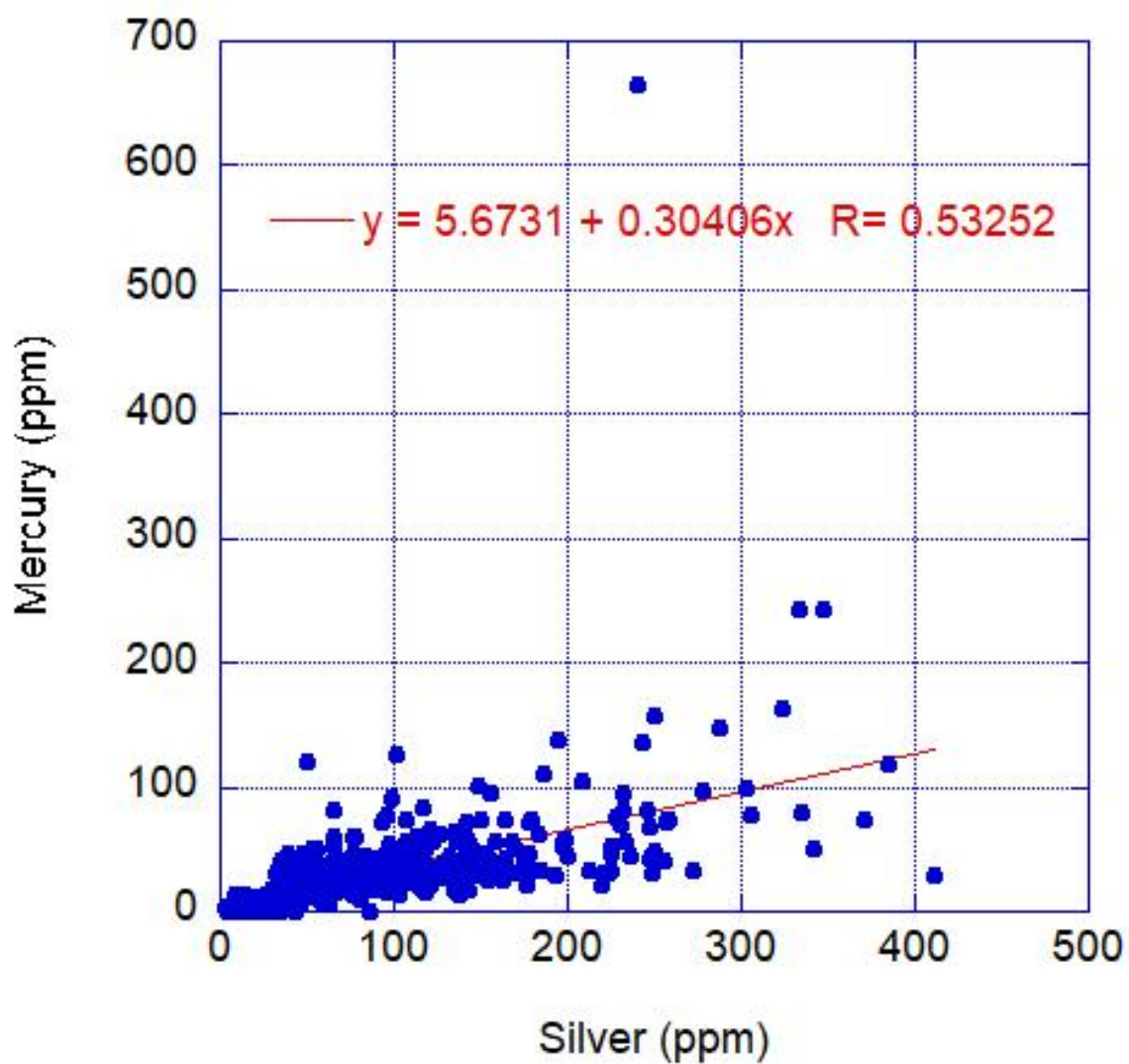


Figure 31. Comparison of Hg to Ag levels in ppm. Heightened concentrations of Hg correlated with increased Ag concentration when below 200 ppm.

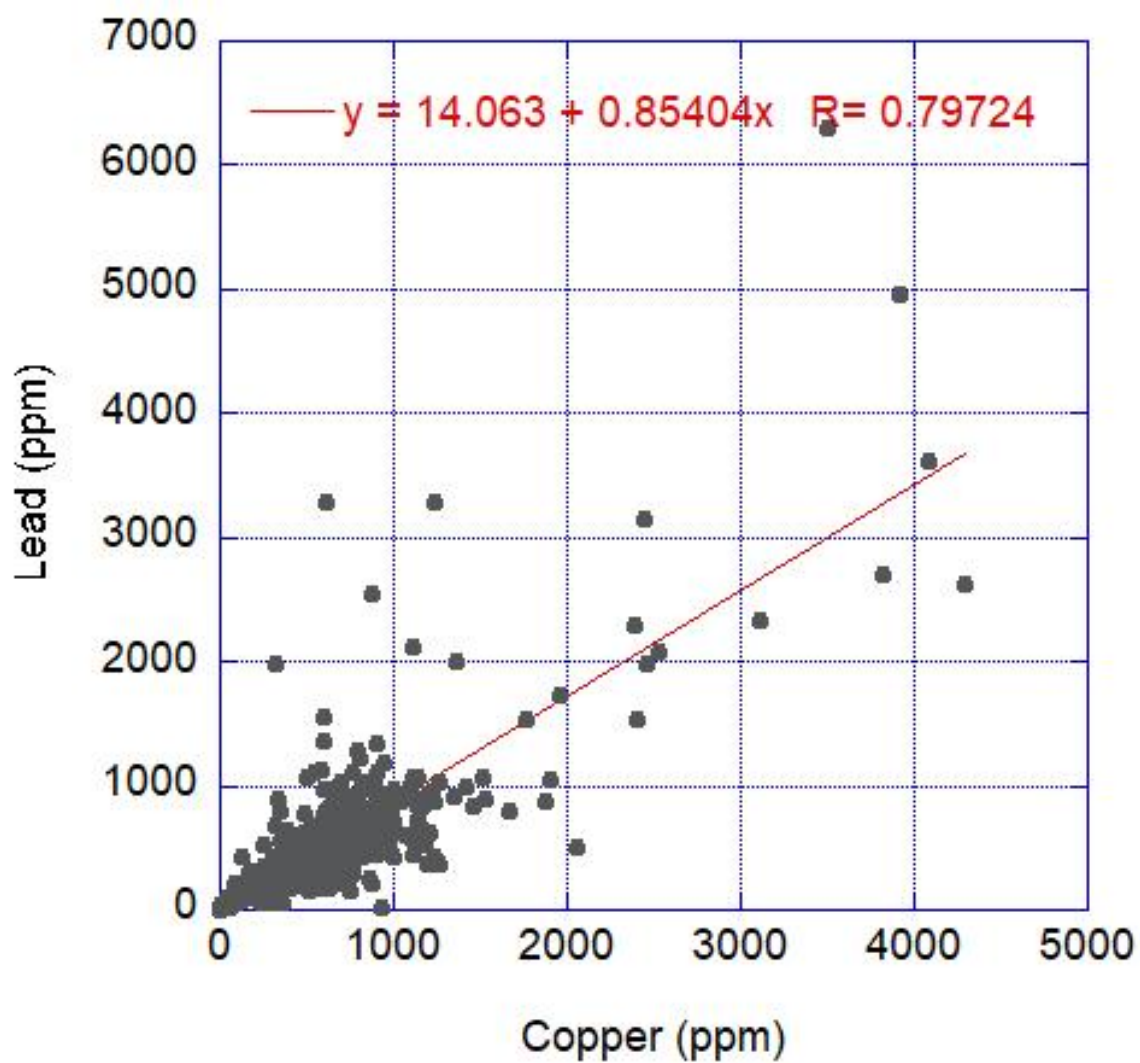


Figure 32. Comparison of Pb concentrations to Cu concentrations in ppm.

With the volumetric analysis of the general tailings and the estimated tonnage of each EOI accounted for, the full impact upon the surrounding environment by these tailings can be calculated. As mentioned earlier, the two chief EOI's are As and Hg, both of which have different detrimental effects on the local ecosystem. Pb, while also of concern, was found to be of least concern when compared to As and Hg because the species found within the tailings was primarily galena (PbS), which was considered to be stable in comparison to the oxidized and more reactive As and Hg species within the tailings. These two elements are also the cause of a myriad of health impacts, which will be covered in the following section. The plausible effects of each element on the local flora, fauna, and natural systems will be discussed, although this topic deserves its own thesis work, since one would be hard-pressed to encompass the full environmental impact of the tailings within a single section. Ag and Cu were also accounted for to better understand their interactions with more toxic elements.

To verify accuracy, the data for the mill site was compared to distributions found in other parts of the Mojave Desert from previous studies, the most common element of study being arsenic. Kim et al. (2014) conducted a very extensive study concerning arsenic distribution from gold and silver mines in the western Mojave Desert, among which Calico was included but given only cursory study in favor of larger arsenic sources far to the west. The study quantified local arsenic distribution at several locations, and within the Calico Mining District three locations were chosen where concentrations were generated from the

tailings piles around the district. These values listed arsenic quantities at 146, 154, and 160 mg/kg depending on the specific tailings pile tested (Kim, 2014).

The gross mass of arsenic within the tailings site was estimated at 33 metric tons spread throughout the site's 2 km by 0.2 km area. The average concentration of arsenic found was 126 ppm, virtually identical to the spot sampling done by Kim et al. (2014). Hotspots in excess of 1,500 ppm As were found at a few select sites in the present study. It is no hyperbole to describe the amount of arsenic present within the Garfield Mill tailings as extreme, considering that the EPA's current drinking-water limit for arsenic is 10 ppb and the soil standard is 0.39 ppm (EPA, 2019). While arsenic is naturally present within geological bodies in the western continental United States, they are normally locked in sulfide mineral form and thus relatively insoluble within the human body. The mining activities conducted at Calico, the processing and increase of surface area during the milling process, and weathering of the tailings over the past 100 years have altered much of the original As mineralogy to more readily mobile oxides.

While the effects of arsenic on the surrounding environment has been studied for some time and in great detail (Abdul, 2015; Chakraborti, 2015), the complex nature of its valency within compounds of sulfur (Basua et al., 2013; Dos Santos et al., 2017), its wide speciation paths from weathering (Corkhill et al., 2013), and its varying stability have only recently become a subject of detailed research (Corkhill, 2009; Hu, 2017; Ma, 2014, etc.). It is possible that the arsenic-bearing minerals within the Garfield Mill tailings underwent varying

degrees of natural weathering by rain over the past century, which could have caused them to speciate into these more mobile compounds. The addition of potassium cyanide, used to leach silver from the tailing, only further complicates tracking its speciation at the Garfield Mill site, since the effect of this compound on sulfide degradation and oxidation is unknown.

XRD analysis has confirmed the presence of arsenopyrite, claudetite, proustite, and realgar (Figures 21 and 22). Arsenopyrite, the most common source of arsenic on earth, often occurs within a range of ore deposits including magmatic, hydrothermal, and porphyry-style systems (Corkhill, 2009). Arsenopyrite is a common mineral associated with both gold and silver deposits, which leads to its extraction and subsequent dumping as solid waste at mining sites. It often occurs alongside other arsenic sulfides such as realgar, while claudetite is the chief product of the combustion of arsenic-bearing minerals and especially sulfides. Depending on environmental conditions, arsenic sulfides can speciate into many different compounds, including but not limited to scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), and various iron hydroxides alongside arsenic (III) and (V) ions (Figure 33).

SEM analysis of collected tailings samples proved effective in characterizing the mineralogy of the Garfield Mill tailings and by extension the Calico Mining District. The analysis of several common minerals such as quartz, sanidine, and chrysocolla under SEM solidifies the findings of earlier mineralogical studies conducted at Calico by individuals such as Lindgren (1887) and Weber (1966). However, detection of As- and Hg-bearing minerals was

limited to a few grains less than 15 microns in size for As-bearing minerals, while no Hg was found in any of the samples analyzed. This result may be an artifact of sample size and distribution and thus require more extensive study to fully characterize the tailings mineralogy. In one scenario, larger quantities of material may need to be examined so that traces of various elements may be identified. Analysis by SEM of the interiors of the tailings piles, possibly requiring drilling equipment and relevant permissions, may yield larger toxic-element findings, since the current levels detected via XRF were surficial and do not account for the concentration of the elements within the tailings piles. Alternative methods such as soil sieving may also prove useful in locating toxic compounds.

SEM analysis found only one instance of an As-bearing mineral being present, but identification was hindered by several factors. The mineral grain in question contained Pb, Sb, Si, S, and S, in descending order of amounts (Figure 23). Calico's hydrothermal formation, the presence of As found in high quantities by XRF, and the presence of As-bearing minerals such as realgar in multiple XRD samples help narrow down the possibilities. The ratio of As to S within this mineral assemblage (As 5.21%, S 9.98%) could identify the mineral as having pockets of orpiment (As_2S_3), a common product of realgar and arsenopyrite weathering. Orpiment is known to form in low-temperature hydrothermal systems like those at Calico and shares common mineral associates with minerals identified at Calico, including galena, realgar, pyrite, barite, and quartz (Mindat.org, 2019). However, this fact does not explain the high Sb presence within the assemblage.

XRD analysis of sample 6 from the Garfield Mill site (Figure 22) displayed multiple 100- to 150-count peaks identified as boulangerite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$). Other XRD samples displayed lower peaks (<50 counts) of boulangerite, while samples such as sample 3 from Sector 1 contained no boulangerite or any other Sb-containing minerals. Boulangerite shares mineral associates with quartz, arsenopyrite, galena, pyrite, and stibnite (Sb_2S_3) (Mindat.org, 2019), making its presence within the tailings matrix plausible. Although stibnite could also be present, the ratio of Sb to S does not favor its formation; the low-temperature hydrothermal systems at Calico would instead favor the formation of boulangerite, which often consists of thin, fibrous, and acicular masses of hair-like crystals. The crystals may have been fragmented during the milling process owing to their brittle nature, resulting in the grains found under SEM. Jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$) could also be present, as it has been found throughout the southwestern Mojave Desert (Mindat.org, 2019), lacks the fibrous characteristics of boulangerite, and shares similar mineral associates with boulangerite, with the addition of barite. However, both jamesonite and boulangerite have a chemical ratio that favors sulfur, which is much lower than Sb and Pb in the SEM sample. Bindheimite may be the mineral found under SEM, as it is a common secondary mineral produced from the oxidation of Sb containing Pb–S minerals (Mindat.org, 2019). Therefore, the SEM grain is probably an Sb–Pb compound that may have been boulangerite, jamesonite, or Sb-bearing galena before being milled, with intrusions of quartz (explaining the Si content in the grain) and realgar/orpiment (accounting for the As and S content within the mineral grain) present.

The speciation of these minerals at the mill site appears to be greatly affected by the combination of potassium cyanide used during the leaching era, rainwater, and ambient weathering by nature. The caustic potassium cyanide (KCN) used during the leaching era of the tailings probably increased the alkalinity of the tailings during processing because of its high pH (9.3–9.5). In a basic environment and under standard pressure and temperature conditions, arsenopyrite would speciate into $\text{Fe}(\text{OH})_3 + \text{As}^{(\text{III})}$ ion or $\text{As}^{(\text{V})}$ ion depending on the electron activity of the system. Realgar would change to Fe^{3+} ion + $\text{As}^{(\text{III})}(\text{aq})$ or $\text{Fe}(\text{OH})_3 + \text{As}^{(\text{V})}$ ion depending on the extent of alkalinity in the tailings. In either case, the arsenic is released from its mineral form and the production of both $\text{As}^{(\text{III})}$ and $\text{As}^{(\text{V})}$ occurs. The now free $\text{As}^{(\text{III})}$ ions could then react with oxygen to form arsenic trioxide/claudeite or react with the various minerals present within the tailings, such as sanidine or galena. In any case the KCN leaching used on the tailings acted as a mobilizer for arsenic, leaving it more susceptible to speciation and mobilization by wind and rainwater.

The effects of rainwater on the arsenic-bearing minerals within the Garfield Mill tailings can be understood by evaluating the speciation of arsenic by slightly acidic rainwater and the effects of hydrogen peroxide (H_2O_2) produced by rainwater on the tailings. Ma et al. (2014) studied the effects of rainwater-produced hydrogen peroxide on arsenic release from arsenopyrite, using H_2O_2 levels commonly found in rainwater. The study confirmed that hydrogen peroxide expedited arsenic release through the formation of FeAsO_4 (scorodite) precipitates from arsenopyrite, changing the arsenic from arsenite

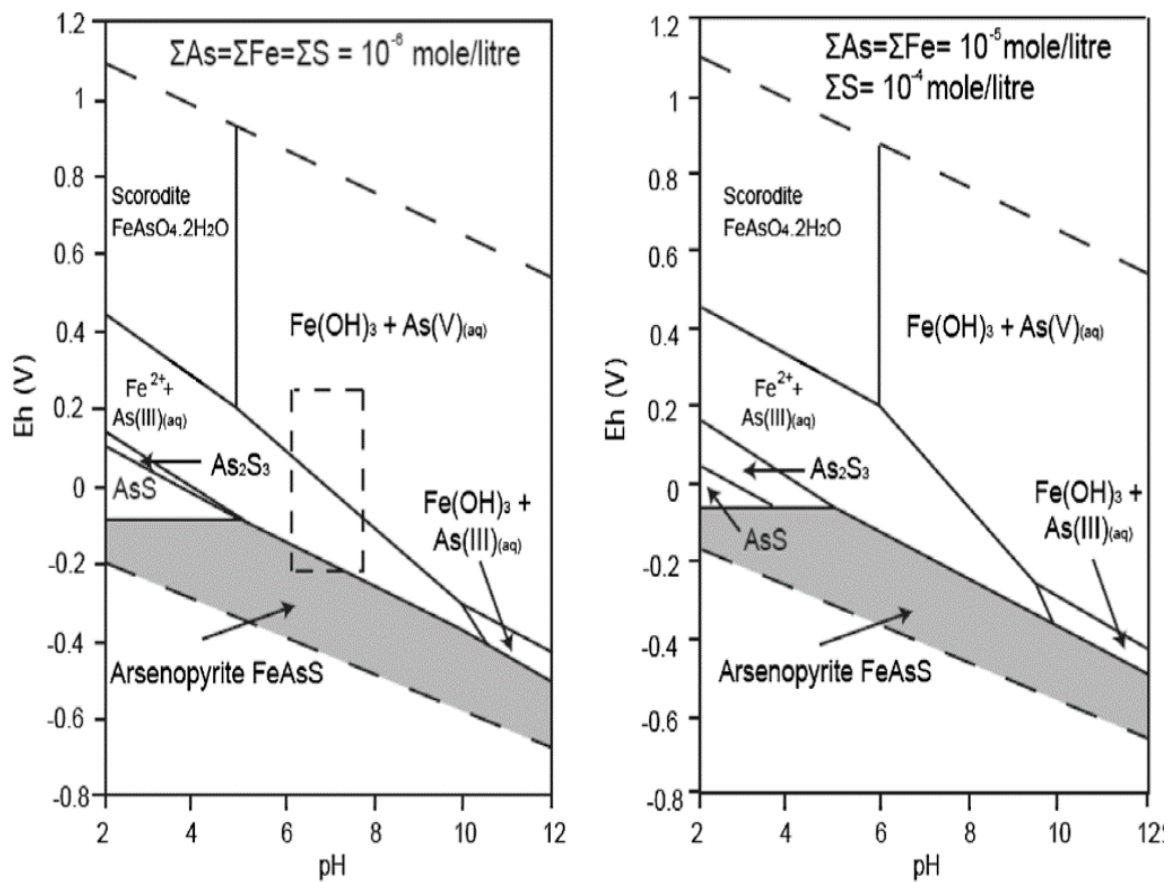


Figure 33. Eh–pH diagrams for the Fe–As–S–O system (25 C, 1 atm) at two concentrations of components. The shaded area shows the stability field for arsenopyrite. The dashed box in the center of diagram on the left-hand side indicates typical near-surface conditions (adapted from Craw et al., 2003) (Corkhill, 2009).

(As^(III)) form to arsenate (As^(V)) form. Again, the prevailing trend of arsenopyrite weathering favors the formation of As^(V) which, while more common in nature than As^(III), exhibits a much lower toxicity with respect to biological processes, which will be discussed in the next section. The weathering of arsenic by rainwater and natural oxidation acts as a medium for mobilization of both stable ionic species of arsenic, though their respective methods of transport differ. In the case of mobilized arsenite it is believed that fluvial transport acts as the primary medium for mobilization owing to arsenite's solubility in water (Kim, 2013). For arsenates, fluvial transport is of less concern because of its very low solubility in water, but this fact does not necessarily equate to its being more stable than its arsenite form, and it may be mobilized through aeolian means instead. Biomethylation of As may have occurred at the site by local plant life, although to an unknown extent; this aspect should be investigated in future works.

Mercury abundance was estimated at 7 metric tons for the tailings site, most of which was concentrated around the original Garfield Mill location within Sector 1. The mercury was imported in pure native form during the milling era, and while the presence of native mercury within the tailings is likely, the presence of organic and inorganic mercury-bearing compounds formed through interactions with the other minerals present within the tailings is of greater concern. Fernando-Martinez et al. (2019) found that sandy soils rich in quartz and feldspar minerals, such as those at Calico, would hold cationic Hg compounds and thus greatly reduce their mobility. This poses the possibility of

the Hg being immobilized owing to the desert soils at the site. Should this eventuality be true, it can be hypothesized that most of the Hg brought to the Garfield Mill stayed within the tailings site, and the threat of mercury-related health risk for the neighboring communities would be lowered. Additional study of the site's mercury inventory would be required to better understand the mobility of the Hg species within the tailings. Also, records detailing the quantities of mercury sold to the various mining operations at the Calico Mining District would prove useful in estimating how much mercury should be expected to be present compared to how much is present at the site. Conversely, this increased bonding with local soils may increase Hg mobility in tailings piles exhibiting less cementation, and thus lower stability, than those that have undergone a greater degree of cementation from local rainwater.

Hg was found to be prone to binding with soils and tailings with smaller grain sizes, such as those exhibited at the Garfield Mill site (Figure 23), which coincides with the findings of Fernando-Martinez et al. (2019). Of the Hg plumes found within the Garfield mill tailings, the three with the highest distribution areas and concentrations were found within Sector 1. Tailings pile 1 of Sector 1 (original site of Garfield Mill) contained few solidified tailings piles and instead contained piles of loose, soft, and fine-grained tailings dust that resembled piles of cake flour in texture. Pile 3 of Sector 1 exhibited a mixture of semi-cemented and "cake-flour" tailings, both of which appeared to have similar grain/particulate sizes. The cake-flour piles exhibited little stability and were easily swept up by the wind while the semi-cemented tailings produced little airborne dust because

of its hard surface crust, which effectively created a protective shell over the tailings piles and trapped the tailings within.

However, this surface crust is easily friable and crumbles under very slight pressure into a fine dust, the encased tailings resembled the cake-flour tailings piles and were similarly swept away by the wind. The small particulate size, coupled with Hg favoring smaller particles to bond with, leaves aeolian transport of Hg as a concern for the tailings site. Although the surface crusts of the semi-cemented tailings piles show little signs of aeolian transport when left undisturbed, anthropogenic factors, primarily local off-roading activities, can easily break the surface crust while simultaneously kicking up the loose underlying Hg-containing tailings dust, mobilizing them in the process. This possibility provides a possible health hazard to both the off-roading enthusiasts and the surrounding residents who breathe in the mobilized dust. It also leads to the next subject of concern, the species of mercury present.

XRD analysis of several collected soil samples identified various species of arsenic and lead alongside the general mineral matrix of the tailings. Hg went undetected under XRD analysis; thus, the identification of mercury species at the site was unsuccessful. Future analysis of the tailings using SEM may prove useful in identifying specific Hg species in future studies. However, the detection of liquid mercury by the above methods is often complicated by volatility when the element encounters a vacuum or a high-energy beam. A likely Hg species present at the site may be native mercury used during mill activities. An unlikely but plausible species may also be found in the mineral calomel (Hg_2Cl_2), also

known as mercurous chloride, owing to the high presence of chloride minerals such as chlorite alongside the ores of Calico. The extraction of silver left little of the original minerals present within the tailings, since when stripped of their silver, many of the chlorides had probably bonded to other minerals present in the mercury amalgam. While these mineral species may very well be locked within the tailings piles, organic Hg species may exist at the site owing to their reactions with local fauna.

Ha et al. (2017) and Fernando-Martinez et al. (2019) discuss the role of plant life on the mobilization of mercury into organic variations such as methylmercury (CH_3Hg^+). The latter is commonly formed by soil bacteria residing in the rhizosphere of plant roots and through interactions with both fresh and salt water (Ha et al., 2017). It is an extremely toxic, organic form of mercury that can reach lethal doses at 20–60 mg/kg of body weight (EPA, 2019). The possibility of methylmercury presence at the site, and the prospect of its mobilization within the tailings dust, would pose a major health risk to the surrounding communities and wildlife, the specifics of which will be covered in the following section. Silver was found in surprising quantity within the Garfield Mill tailings (Figure 24), to the extent that it may prove useful for defraying costs of future remediation efforts. Although milling and remediation costs would probably be too great to be covered completely, extracting the Ag, Zn, Ba, and Cu within the tailings may prove useful in lowering project costs.

Future remediation work should (1) account for the biomethylation of As and Hg, (2) reduce aeolian and fluvial mobility, and (3) either increase the

stability of the tailings or remove them entirely. Transport of arsenic by wind is the chief concern for reducing its mobility. The transported form will probably be As^(V) with a much lower toxicity than the arsenic minerals within the tailings, which underwent less weathering than the surface tailings and still contain primarily As^(III). The mercury at the Garfield Mill site is probably transported by aeolian means but may also pose a concern for local groundwater owing to its proximity to wells.

Overall stability of the Garfield Mill tailings is variable. Sector 1 contained primarily semi-cemented piles accompanied by pockets of cake-flour piles. Sector 3 also contained semi-cemented piles, but also more cake-flour piles, while pile 3 of Sector 3 displayed moderate cementation second only to that found in Sector 4. These easily transported cake-flour piles leave Sectors 1 and 3 as the highest health concern; they should be the first to undergo remediation should any such projects be undertaken in the future. Sector 2 contained waste-rock piles and some shallow (less than a few centimeters thick) semi-cemented piles and produced very little dust when local winds grew in intensity. Sector 4 is of least concern owing to the heavy cementation and subsequent increased stability of the tailings. The Behemoth Mound produced little to no dust during foot traffic during field work, with small exceptions occurring just south of the Mound, where the tailings exhibited a more semi-cemented structure. This condition is probably due to Sector 4 having undergone cyanide leaching, which may have aided in further cementing the tailings.

Health and Environmental Impacts on Surrounding Airshed

Amid the myriad of concentrated minerals within the Garfield Mill tailings, those containing arsenic, lead, and mercury are among the most toxic to human health. Heightened levels of airborne arsenic- and mercury-laden dust could affect the health of Barstow, Dagget, and Yermo citizens if left unremediated. Transport and infiltration by fluvial means could also bring local groundwater purity into question depending on the depth of the water table. The silver content of the tailings, while not a major health risk, could still cause respiratory issues and discoloration of the eyes and skin if an individual were exposed to large quantities. The presence of airborne lead could also endanger the respiratory and neurological health of children and older adults within these communities.

Kim et al. (2014) found that several of the tailings piles at Calico generated dust that could cause both cancer- and non-cancer related health risks exceeding the minimum risk level for arsenic exposure and could also increase such health risks within the surrounding area. The main route of exposure was found to be inhalation and the subsequent accumulation of arsenic-bearing particles within the fluid lining of the lungs. For particles that cannot be absorbed through the alveoli into the bloodstream, the health risk would consist of a buildup of particulates within the lung fluid and an increase in lymphatic fluid within the lungs to expel the foreign matter. This condition would lead to coughing and difficulty breathing, while individuals with compromised/weakened immune systems (i.e., children and older adults) could experience symptoms so severe as to require hospitalization. Particulates that can pass into the

bloodstream could subject individuals to symptoms of arsenic poisoning (fatigue, hormonal imbalances, degradation of nerves, etc.), bloodstream pH imbalance, and disruption of the endocrine system. Health risk falls with increased proximity to the site, but individuals located as much as 64 km (40 mi) from the site are still at risk, especially on windy days (Kim et al., 2014).

Although XRF confirmed the presence of mercury, the XRD analysis of soil samples from the Garfield Mill site were devoid of any mercury signal and no mercury compounds were identified. Determining the specific mercury species in the tailings material would probably require SEM analysis or concentration of analysis samples via gravity (e.g., use of a gold pan). The presence of mercury in the tailings is nonetheless confirmed by XRF findings and still poses a health risk to the surrounding airshed. Owing to the varying reactions paths mercury exhibits in conjunction with fresh and playa saltwater, transport by water is considered a primary mode of potential transport for mercury at the Garfield Mill site. Local Mojave River Groundwater (MGW) Basin levels range from 51.8 m–64 m (170–210 ft) below the ground surface around Calico and Yermo while resting at 30–45 m (100–150 ft) within Barstow (USGS, 2019). The threat of groundwater contamination by mercury at Barstow is considered low based on MGW data from the U.S. Geological Survey. The 30-m (100-ft) difference in average MGW surface depth generates a large drop, or possibly a cone of depression, within the Calico Yermo section of the MGW basin. MGW flow would then trend east towards Yermo based on these levels, leaving Barstow at a lowered risk of MGW

contamination. Barstow's susceptibility to mercury intrusion within the local MGW basin should be investigated in a separate study.

Future Work

This study was intended to act as a benchmark for future work at Calico and tailings sites with similar cases of arsenic- and mercury-laden tailings. While the study has addressed volumetrics, stability, chemical distribution, and some mineralogy of the Garfield Mill tailings, many other topics remain for future analysis, such as further identifying the mineralogy of the tailings, methods and extent of transport of the tailings by wind and water, speciation of As and Hg within the tailings, and remediation of the site.

Investigation into the mineralogy of the tailings suffered from numerous limitations. Time and instrument constraints made it difficult to identify Hg species unambiguously. This constraint was further exacerbated by XRD's inability to identify Hg. Much more work will probably be required to properly identify the species of mercury present within the tailings. XRD did identify mineral species of As and Pb, giving insight into the minerals originally present at the site that had been left undocumented. However, further studies should be undertaken to identify As and Pb species within the tailings piles, since samples taken for this study constituted only the surface and the first few centimeters of tailings underneath the surface crust. It is entirely possible that the rate of weathering on the tailings surface has changed considerably in comparison to the interior

mineralogy, and this possibility should be investigated to better understand the interior chemistry of the tailings.

The transport of the Garfield Mill tailings by wind and water, while touched upon in this study, is deserving of its own independent study considering its importance to the public health of surrounding communities. Mirroring methods used in studies such as Kim et al. (2015) would probably be beneficial in such a study. Transport by wind is the primary means of mobilization for the tailings, making investigations into the ambient air quality of the local airshed a priority. Analysis of local groundwater through well tests should be undertaken to better understand local groundwater flow, estimate the possibility of contamination by As or Hg, and predict which communities are at a higher risk of groundwater contamination. Investigations into local soil transmissivity and contaminant movement rate would also be of benefit to better understand the tailings' effects on local MGW purity.

A study focusing on the weathering of the tailing minerals and subsequent thermodynamic reactions with the surrounding environment would aid in fully grasping the stability and toxicity, or lack thereof, of the Garfield Mill tailings. This study discussed which weathering products were most likely to be present given the processes to which they were subjected. Doing so would allow local governing bodies to better assess the health risk posed by the tailings, in both their present and future forms, which could mitigate future cleanup costs (if not eliminate them) should the tailings prove to be weathering into minerals of lesser

toxicity. This project could be undertaken alongside the previously mentioned mineralogical study of the tailings' interiors.

Various remediation techniques, both experimental and industrial, discussed in the previous section may prove beneficial for future remediation of the Garfield Mill tailings. In its current state the site may provide an excellent area for testing experimental remediation techniques and their effectiveness on As and Hg removal/stabilization; it could also be used to demonstrate the effectiveness of previously tested techniques on a larger scale than what may have been undertaken in original studies. Other studies referenced earlier may prove that remediation may be unnecessary, and that leaving the tailings as they are could be the best solution.

CHAPTER FIVE: CONCLUSIONS

The Garfield Mill tailings at Calico, California, resulted from a once-booming silver mining district that existed from the 1880's to the early 1960's. Because of inferior extraction techniques, historically poor safety guidelines, and a general lack of environmental awareness, large quantities of arsenic and mercury deposited with the tailings material were left to be weathered, mobilized, and transported by biotic and abiotic processes. Mercury was used as a chemical amalgam in the extraction of silver, while arsenic was naturally present in local ore. Following the mining era that centered on stamp milling and mercury amalgamation, activity in the district slowed owing to decreased silver output, increased processing costs, and a decline in silver prices. Activity in the district was renewed in the 1930's to 1950's, when modern cyanide leaching techniques were used to extract more silver from the southern sections of the Garfield Mill tailings, techniques that acted to mobilize the arsenic-bearing minerals locked within them.

This study focused on establishing the volumetrics of the tailings and making an elemental inventory of them; it also assessed the breadth and depth of the toxic elements they contained. To achieve this goal, geochemical distribution data was extracted with a Niton portable XRF analyzer; this data was then used to produce chemical concentration maps, and deposit-thickness data was used to generate an isopach map. The data was processed using various items of mapping software such as Agisoft Photoscape and RockWorks¹⁷. These maps allowed the interpretation of chemical distribution, concentrations,

trends, and volumetrics within the mill tailings, encompassing a site that was 2 km long and 0.2 km wide just south of Calico Ghost Town across from Old Ghost Town Road. With the help of Dr. Kerry Cato, aerial drone photographs were taken to create a 3D orthomosaic map of the site, which was then uploaded to Google Earth and overlain with the various chemical concentration maps to pinpoint areas of concern at the site.

The total mass of the Garfield Mill tailings was calculated to be 268,000 metric tons. The two main elements of interest were As and Hg, while Ag, Zn, Ba, Pb, and Cu were also examined to understand their interactions with more toxic elements. Concentration of As averaged 141.3 ppm, with a high of 1,800 ppm at its greatest concentration within pile 3 of Sector 1, with a total mass of 33.2 metric tons. Hg concentrations averaged 36.75 ppm, with the highest concentration being 664.12 ppm around the foundation of the original mill site in Sector 1, with an estimated mass of 7 metric tons. Concentrations of Ag averaged 95.1 ppm (3.06 opt), with a total mass of 17.9 metric tons. Assuming a price of \$15.42/troy oz, approximately \$8.8 million of potential revenue may be present within the mill tailings, which could provide a means of reducing the costs of future remediation projects. Since similar results were found for Ba, Cu, and Zn, recovering these elements could also provide additional revenue to cover remediation project costs.

It is highly possible that the current surficial geochemical scans of the tailings represent only the minimum amount to be found at Calico. Considering Calico's geology, which favors rich silver deposits closer to the surface, the

assay value of which became poorer with increased depth, the first years of mining at Calico probably yielded the greatest amount of silver. Since no clear organization or management of the tailings were ever identified or documented, it can be assumed that the tailings are layered chronologically, with the surface being the youngest material while the interior, deeper material is older.

Therefore, the elemental mass estimates listed earlier are considered minimum values, while the interior of the tailings probably contain more silver, arsenic, and mercury.

Distribution patterns of As, Ag, Zn, and Pb were similar, probably because of the effects of As and Pb on the mercury amalgam, which caused it to coagulate and hemorrhage vast quantities of tailings materials when present, greatly reducing Ag extraction. Sector 1 had the highest concentrations and widest distributions because it was the location of the former mill site, while Sector 4 had the lowest concentrations of all elements, probably because the southernmost sections of the site were subjected to cyanide leaching. This process increased the cementation and stability of the processed tailings, such as the Behemoth Mound of Sector 4 (a rock hammer was required to break it). The other sectors exhibited mild to light cementation of the tailings piles, usually in the form of a thin surface crust that was easily friable when subjected to minor pressure. Sectors 1 through 3 also contained piles of “cake-flour” tailings that were easily swept by wind and had undergone little to no cementation. While the tailings are relatively stable, local off-roading activities increase the risk of aeolian

transport of the tailings by breaking the surface crust and kicking up the cake-flour tailings held within.

Transport of As and Hg within the tailings was believed to be primarily aeolian, while fluvial transport remained a concern owing to the shallowness of the local water table. Fluvial factors have probably changed the As-bearing minerals within the tailings into more mobile variants, probably a mixture of iron hydroxides and free As^{III} and As^V ions. Mercury may have undergone biomethylation, thus becoming more mobile via wind owing to the presence and processes of local flora, but this possibility requires a separate investigation. A study of the outlying areas of Yermo and Barstow would help characterize transport trends of the tailings and quantify the health risks to which the local populace may be subjected.

It is plausible that there are errors within the data collected here, especially because of hardware malfunctions in the field due to the high temperatures at the tailings site. On several occasions the Niton analyzer exhibited system freezes and experienced shortened battery life when temperatures exceeded 100° F. Although a simple reset of the analyzer appeared to resolve the issue and no noticeable discrepancies were found within a set of data points taken after such incidents, it is still possible that readings could have been off by a few ppm. Re-scanning of reference standards revealed no significant drift in calibration following these errors. Contamination of the site by foreign soils is also a concern, since frequent local off-roading activities may have spread tailings from different sectors within the site to other sectors. It is

therefore possible that some data points could be inaccurate, such as those taken in proximity to service roads. Off-roading activities could have also introduced soil material from other areas; although such contamination would probably be minimal, it should nonetheless be taken into consideration.

Future studies may benefit from analyzing more soil samples from the tailings to better understand their mineral composition both at their surfaces and within their depths. SEM analysis, among other tests, would prove useful to future studies to help characterize the mineral species present within the tailings (such as mercury species) that XRD could not detect. Testing local groundwater for increased mercury and arsenic levels would prove useful in characterizing the spread of the tailings through fluvial means and to better understand any groundwater risks. Future remediation of the site is highly recommended owing to the extreme levels of arsenic and mercury present, both of which lie well above the EPA's soil and water standards (EPA, 2019).

The Garfield Mill tailings are stable around the southern end of Sector 3 and all of Sector 4, while Sectors 1 and 2 were less cemented and more prone to mobilization by wind. Future remediation projects should focus on Sector 1, in particular piles 1, 3, and 5, owing to the high concentrations of toxic elements within the poorly to semi-cemented tailings piles. Sector 2 should follow, owing to the presence of "cake-flour" tailings, though the extent of As and Hg within it is much lower than in Sector 3. Sector 3 had both elevated As concentrations and increased cementation in many of its tailings piles. Should project funding be limited, Sector 3 should be remediated before Sector 2 owing to its toxic element

content. Sector 4, the Behemoth Mound, contained very few toxic elements content and its tailings were the most stable of the entire site; thus it could be remediated last, although the interior of the roughly 4-m-tall mound should be tested to ensure that the levels within the interior tailings match those of the surface. However, extracting the silver within Sector 4 may prove useful in reducing project costs, and the same is true for Sectors 1 and 3 thanks to their tailings' high silver content, while Sector 2 had the lowest silver content and thus would be less productive.

Overall, remediation of the Garfield Mill tailings is recommended, but future activities would benefit from additional health-risk studies and further investigation of the mineral speciation within the tailings. The tailings pose a health risk to the surrounding populace owing to the high winds in the area, and their proximity to Interstate 15 poses a hazard to those who frequent it. Remediation of the As and Hg within Sectors 1 and 3 should take priority, and future studies should take place during the winter or spring to avoid extreme temperatures that cause equipment to malfunction.

APPENDIX A

Field Niton XRF Geochemical Concentration Data

Reading	Time	LATITUDE	LONGITUDE	Pb	As	Hg	Zn
1036	8/14/2018 11:14	34.94088	-116.86485	46.72	31.2	<LOD	80.27
1037	8/14/2018 11:24	34.94084	-116.86459	59.11	27.27	<LOD	112.42
1038	8/14/2018 11:28	34.94076	-116.86437	58.94	15.45	<LOD	75.75
1039	8/14/2018 11:33	34.9407	-116.8642	413.99	56.37	14.76	197.55
1040	8/14/2018 11:37	34.94067	-116.86402	679.67	224.44	31.81	555.44
1041	8/14/2018 11:42	34.94064	-116.8638	532.08	144.17	45.2	218.93
1042	8/14/2018 11:48	34.94063	-116.86362	517.54	154.28	28.83	258.91
1043	8/14/2018 11:53	34.94054	-116.8635	432.82	63.55	44.39	194.05
1044	8/14/2018 11:58	34.94053	-116.86328	779.21	335.1	25.78	222.71
1045	8/14/2018 12:03	34.94045	-116.86305	175.71	56.95	30.5	383.52
1046	8/14/2018 12:04	34.9404	-116.86287	188.79	<LOD	<LOD	137.17
1047	8/14/2018 12:08	34.9404	-116.86286	237.51	72.02	20.11	129.68
1048	8/14/2018 12:12	34.9404	-116.86261	2548.75	1133.82	24.18	212.66
1049	8/14/2018 12:17	34.94021	-116.86267	180.19	56.74	10.11	138.91
1050	8/14/2018 12:22	34.94026	-116.86286	217.18	44.07	17.25	148.17
1051	8/14/2018 12:27	34.9403	-116.86307	243.91	48.29	20.69	146.02

REFERENCES

- US Bureau of Mines. (1993). Year Books 1932-1993. *US Government Printing Office*.
- Abdul, M. (2015). Arsenic and human health effects: A review. *Environmental Toxicology and Pharmacology V.40*, 828-846.
- Agey, W. W., Batt, J. V., Wilson, H. W., & Wilson, W. J. (1973). Beneficiation of Calico District, California, Silver-Barite Ores. *US Bureau of Mines Report of Investigations 7730*, 1-13.
- Basua, A., & Schreiberb, M. E. (2013). Arsenic release from arsenopyrite weathering: Insights from sequential extraction and microscopic studies. *Journal of Hazardous Materials 262*, 896-904.
- Berry, J. (2017). Silver production and reserves from the Silver King Vein, Calico, California: A forensic geology approach. *CSUSB Thesis Database*.
- Chakraborti, D. (2015). Groundwater arsenic contamination in Bangladesh—21 Years of research. *Journal of Trace Elements in Medicine and Biology V.14*, 237-248.
- Chowdhury. (2018). Physiographical variability in arsenic dynamics in Bangladeshi soils. *Science of the Total Environment V.23*, 1365-1372.
- Collins, H. F. (1891). Metallurgy of Lead and Silver. *Royal School of Mines Treatise on Metallurgy*, 80-111.

- Corkhill, C., & Vaughan, D. (2009). Arsenopyrite oxidation – A review. *Applied Geochemistry* 24, 2342-2361.
- Dos Santos, E., Lourenço, M., Pettersson, L., & Duarte, H. (2017). Stability, Structure, and Electronic Properties of the Pyrite/Arsenopyrite Solid–Solid Interface–A DFT Study. *Journal of Physical Chemistry*, 8042-8051.
- EPA. (2019). Arsenic Guidelines . *EPA.gov*.
- Fangping, Y., Jintie, L., Tao, X., & Meifang, X. (2018). Arsenopyrite removal from pyrite concentrate using pulsating high gradient magnetic separation. *Results in Physics* vol. 10 , 822-826.
- Fernández-Martínez, R., Esbrí, J. M., Higuera, P., & Rucandio, I. (2019). Comparison of mercury distribution and mobility in soils affected by anthropogenic pollution around chloralkali plants and ancient mining sites. *Science of The Total Environment* vol. 671, 1066-1076.
- Google Earth. (2018). Software sued for mapping and georeferencing data.
- Ha, E. (2017). Current progress on understanding the impact of mercury on human health. *Environmental Research* V.152, 71-86.
- Holland, H. D., Lollar, B. S., & Turekian, K. K. (2005). Geochemical Behavior of Arsenic and Mercury . *Environmental Geochemistry (Vol. 9)*.
- Ilhwan, P., Tabelin, C., Kagehiro, M., & Kensuke, S. (2018). Suppression of the release of arsenic from arsenopyrite by carrier-microencapsulation using Ti-catechol complex. *Journal of Hazardous Materials* vol. 344, 322-332.

Jessey. (2010). *Stratigraphy of the Calico Mountains*.

Kim, C. (2014). Windborne transport and surface enrichment of arsenic in semi-arid mining regions: Examples from the Mojave Desert, California. *Aeolian Research V.14*, 85-96.

Kitae, B., Do-Hyung, K., Sung-Woo, P., Byung-Gon, R., Tserennyam, B., & Jung-Seok, Y. (2009). Electrolyte conditioning-enhanced electrokinetic remediation of arsenic-contaminated mine tailing. *Journal of Hazardous Materials V. 161 Issue 1*, 457-462.

Lane, L. B. (1993). *Calico Memories of Lucy Bell Lane*. Calico.

Lindgren, W. (1887). The Silver Mines of Calico, California. *Scranton Meeting*, 717-736.

McLachen, & Gray. (1933). The MacArthur-Forrest Cyanide Process. *Journal of the Chemical, Metallurgical and Mining Society of South Africa.*, 375-397.

Mindat.org. (2019, March 3). Retrieved from Mindat.org: <https://www.mindat.org/>

Ochart, T. (2015). Post-mining estimation of silver production from the Silver King vein at Calico, California . *California State University, San Bernardino*, 27 p.

State Mineralogist of California. (1879-1925). Report of the State Mineralogist of California . *State Printing Office, Sacramento, CA*.

Thermo Scientific. (2013). Thermo Scientific Niton XL3t GOLDD+ Series Environmental Analyzers.

USGS. (2019, April 15). *Mojave Water Data*. Retrieved from USGS California Water Science Center: <https://ca.water.usgs.gov/mojave/mojave-water-data.html>

Vredenburg, L. M. (2013). Calico. A Brief Overview of Mining History. *Bureau of Land Management*, 7.

Weber, F. H. (1966). Silver Mining in Old Calico. *Mineral Information Service V.20 N.1*, 3-11.

Weeks, F. B. (1929). The Calico Mining District. *Mining and Metallurgy V.10*, 531-534.

Woodburne, M. O., Tedford, R. H., & SWISHER III, C. C. (1990). Lithostratigraphy, biostratigraphy, and geochemistry of the Barstow Formation, Mojave Desert, southern California . *Geological Society of America Bulletin*, 102(4), 459-477.

Xiaoxiao, H., Cai, Y., & Yang, Z. (2017). Hydrothermal alteration of arsenopyrite by acidic solutions. *Applied Geochemistry* 77, 102-115.

Yingqun, M., Yanwen, Q., & Chuxia, L. (2014). The role of rainwater-borne hydrogen peroxide in the release of arsenic. *Chemosphere* 101, 349-353.

